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DETERMINATION/VALIDATION OF TECHNOLOGIES
FOR TREATMENT/RECYCLE OF CONTAMINATED
SLUDGES: PHASE II – FIELD TESTS

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13. ABSTRACT (Maximum 200 words) The Air Force Air Logistics Centers (AF-ALCs) generate large quantities of sludges from their industrial wastewater treatment plants (IWTPs). While these sludges are not toxic based on toxicity characteristic leachant procedure (TCLP) values, these are still classified as "F-waste" (e.g., F002, F005, F006) since the waste waters originate in plating and other metal finishing operations. The Acurex-Battelle Team (ABT) was contracted by the Air Force Research Laboratory (AFRL/MLQ) to identify and evaluate technologies to minimize the volume of these sludges. This report covers the Phase II field tests for: dewatering by flocculation and filtration; metals removal by Liquid Ion Exchange (LIX); Alternative Chemistry of Impurity Based Solids Contact Clarifier Blanket; and Low-Temperature Sludge Drying (Dehumidification). The results of flocculation and filtration testing at WR-ALC were very positive and justify full-scale implementation of the process to economically reduce sludge disposal at WR-ALC by 92 tons/year. The LIX tests at WR-AL showed that the implementation of the anion LIX (A-LIX) process to remove CrVI has the potential to reduce sludge generation at WR-ALC by 276 tons/year. Its scale-up and implementation is recommended. The tests on alternative metal precipitation chemistry at OC-ALC indicated that the use of chemicals to precipitate CrVI and metals can be significantly reduced. It was also determined that dibasic sodium phosphate is a good polishing agent for CrII. However, additional pilot testing is needed to optimize the process.				
14. SUBJECT TERMS Industrial Waste Water Treatment Plant (IWTP) Sludge Reduction, IWTP Sludge Treatment, IWTP Sludge Recycle, Metal Hydroxide Sludges Reduction, Biosludge Minimization, Sludge Dewatering and Drying, Ion Exchange for Metals Removal.			15. NUMBER OF PAGES 144	
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PREFACE

This report represents the results of work done by Battelle in Columbus, Ohio, and ARCADIS Geraghty & Miller, Inc., in Mountain View, California on the Phase II Field Tests for "Treatment/Recycle of Contaminated Sludges", Contract No. F08637-95-D6003, Delivery Order 5300, with the Air Force Research Laboratory, Tyndall AFB, Florida.

The report covers the period of performance from May 1996 to January 1998, focusing on field tests of selected technologies to minimize the amount of sludge requiring off site disposal. Our team's efforts were enhanced through support of others. We would like to express our appreciation to Freddie Hall, Alison Chirkis, Joe Gard, and the IWTP staff of OC-ALC, Shawn Politino, Ellen Griffith, Bill Fennell, and the IWTP staff of WR-ALC, and Dave Vidic of OO-ALC for their assistance.

EXECUTIVE SUMMARY

A. BACKGROUND

The Air Force Air Logistics Centers (AF-ALCs) generate large amounts (300,000 to 1,000,000 gallons/day) of industrial waste waters that must be treated onsite to reduce the toxic (RCRA) metals; total suspended solids (TSS); fat, oil, and grease (FOG); and other toxic organic contaminants contributing to biological oxygen demand (BOD) and chemical oxygen demand (COD). The presence of solvent- and metal-bearing effluents from plating and metal-finishing shops leads to the formation of large quantities of "F-waste" (e.g., F002, F005, F006) in this waste water. As such, these sludges are classified as hazardous waste and are, therefore, expensive to dispose of.

In general, the AF-ALCs produce three basic types of industrial waste water treatment plant (IWTP) sludges: (a) metal hydroxide sludge; (b) biotreatment sludge (biosludge); and (c) oily sludge. However, often these sludges are mixed together and disposed of as a combined sludge.

B. OBJECTIVE

The objectives of this project were to:

- Identify and characterize the problematic IWTP sludges at various AF-ALCs
- Identify current and potential technologies for resource recovery, volume reduction, and/or detoxification of these IWTP sludges
- Evaluate suitable technologies through laboratory pilot-scale testing at an AF-ALC
- Recommend technology prototyping and implementation

A two-phased approach was used to meet the above objectives. This report documents the Phase II efforts to evaluate candidate technologies in pilot-scale tests at three ALCs.

C. APPROACH

The two-phased approach established seven tasks in Phase I to identify the sludge treatment/recycle needs at AF-ALCs and to evaluate and test candidate technologies on a laboratory scale. Available data were collected from each of the five AF-ALCs to establish the quantity, composition, associated disposal cost, and source of the IWTP sludges. Additional

samples were collected and analyzed to characterize the sludges. A literature review and technology selection effort identified potential technologies for each need. The technologies were ranked using a multiple attribute analysis based on technical and economic criteria. Laboratory testing established the potential waste reduction and cost savings that could be achieved with the candidate technologies and sludge streams. The Phase I results are described in the Phase I project report. These tests were used to further establish the recommended technologies and sites for pilot testing during Phase II.

This report summarizes field testing (Phase II) of four technologies at three ALCs. Topical reports on each technology/test provide complete details. These technologies and pilot plant test locations are:

- Flocculation/Filtration at Warner Robbins ALC
- Chromium/Metal Removal by LIX at Warner Robins ALC
- Alternative Precipitation Chemistry at Oklahoma City ALC
- Low Temperature Sludge Drying at Ogden ALC

D. SUMMARY OF KEY FINDINGS

1. Sludge Flocculation and Dewatering, Pilot-Plant Tests

The objective of this task was to perform a pilot-scale evaluation of the effectiveness of two anionic emulsion flocculants (Cyttec 1820A and Nalco 7768) in allowing effective dewatering of IWTP sludge by a filter press without the need for lime addition. If lime addition can be eliminated, the weight of sludge requiring disposal can be significantly reduced, with attendant disposal cost savings.

The evaluation tests were performed in pilot plant dewatering equipment set up at the Warner Robins Air Logistic Center (WR-ALC) IWTP. The tests were conducted using a 470-mm (1.5 ft by 1.5 ft) JWI plate-and-frame filter press fed with flocculated sludge at pressures from 100 to 180 psi.

Test results showed that IWTP sludges could be effectively dewatered without the use of lime. The feed sludge (without lime addition) was readily handled. The filter cakes were firm, allowing easy removal from the filter press. No evidence of cloth blinding was observed.

The test data showed that the dewatered cake solids content of the WR-ALC IWTP No. 2 sludge, and of the combined No. 1 and 2 sludge, could be increased by 4 to 5 percent solids over an unflocculated sludge. The filtrate contained less than 0.2 percent suspended solids and less than 0.1 percent dissolved solids. Filter cakes containing 31 percent solids could be produced, without lime addition, by adding Cytec 1820A to the IWTP No. 2 sludge at 15 lb/ton dry solids, or by adding Nalco 7768 to the combined IWTP No. 1 and 2 sludge at 18 lb/ton dry solids.

A conceptual plant design and economic analysis showed that the sludge quantity can be reduced by about 92 tons/year (i.e., 16 percent of current quantity) at a net cost savings of \$32,000 per year. This estimate is conservative, as we have not taken into account the savings in cost of lime and labor associated with a manual operation for adding lime. The purchased equipment cost was estimated to be \$23,000, which corresponds to a fixed capital investment of \$64,400 using a factored-costing approach. The equipment needed to implement the process is essentially the polymer preparation, feeding, and in-line mixing system. The actual equipment cost may be lower than the estimate as the IWTP No. 2 plant is going through modifications and already has a polymer blending and feeding system under procurement. After this upgrade, only the IWTP No. 1 plant will need a polymer system.

Based on test results, proceeding with the modification of the IWTPs at WR-ALC to incorporate the addition of the flocculants tested is recommended.

2. Chromium Removal by Anion Liquid Ion Exchange and Metal Removal by Mixed Oil Skimming

The objective of this task was to demonstrate at a pilot scale the application of two liquid-liquid extraction technologies, Anion Liquid Ion Exchange (A-LIX) and Mixing/Oil Skimming (MOS), in removing toxic heavy metals from industrial wastewater streams.

The field trials took place at WR-ALC, using effluent from the chromium-plating sump discharged to IWTP No. 2 at the ALC. Current operational practice is to treat industrial wastewater using metal hydroxide precipitation with ferrous salts and caustic, creating large amounts of solid waste. The use of A-LIX and MOS technologies would recover the chromium and other metals without creating high volumes of iron containing sludges. There is then the possibility of recycling and/or reusing these metals. The pilot plant tests at WR-ALC demonstrated that:

- A-LIX implementation at WR-ALC has the potential to reduce waste sludge generation by 276 tons per year
- The A-LIX system has excellent Cr^{VI} removal abilities. Effluent from the system was consistently below 50 ppb, for feed concentrations that averaged 6-ppm.
- The A-LIX system could produce a concentrated Cr^{VI} product of at least 20,000-ppm without disrupting the production of the <50-ppb effluent
- The MOS system involves complex reaction pathways and kinetics, and will require additional engineering before it can consistently extract and concentrate Cr^{III}

With the success of the A-LIX pilot plant operation, it is recommended that either Tinker ALC, Hill ALC, or Warner Robins ALC be chosen as the site for construction of a prototype A-LIX unit. (At Tinker or Hill, the A-LIX system would take the place of the current Cr^{VI} pre-treatment systems.) The unit would be fully automated for commercial use, and would require minimal operator attention. This prototype unit would be used to generate long-term continuous performance data, and generate Cr^{VI} concentrate for reuse/recycle evaluation. From this system, detailed design and economic analysis could be developed, so that "turn key" units and operational procedures would be available to other sites.

3. Alternative Chemistry of Impurity Based Solids Contact Clarifier (SCC) Blanket for Removing Toxic Metals

The objective of this task was to evaluate changes in the process chemistry employed in the solids contact clarifier (SCC) blanket process for removing toxic metals from IWTP sludge. The changes tested were reduced ferrous sulfate addition, pH control using a borax buffer, sodium phosphate addition for enhanced trivalent chromium removal, and insoluble starch xanthate (ISX) addition as a polishing agent for enhanced divalent metal removal.

The field tests were performed at the Oklahoma City Air Logistic Center (OC-ALC). A pilot-scale SCC, designed to treat 25 gpm of waste water, was fabricated and set up at OC-ALC to continuously treat the south equalization basin effluent at the base's IWTP. The pilot plant included three mixing tanks for process chemical addition followed by a 6-foot-diameter SCC. Results of the field tests showed that:

- The ferrous sulfate concentration in a waste water mix tank can be reduced from 21 mg/L to 8 mg/L with no significant decrease SCC blanket removal of Cr^{VI}, total Cr, Pb, Ni, Cd, Cu, or Zn
- Use of borax for pH control was ineffective in enhancing SCC blanket metals removal
- Addition of sodium phosphate to the treated effluent is an effective means of increasing SCC blanket total Cr removal
- Addition of ISX as a polishing agent at an effluent concentration of 6 mg/L improves SCC blanket removal of Cd and Ni

Based on test results, it is recommended that the adoption of the SCC blanket technology be considered for more widespread Air Force use. Ferrous sulfate use can be reduced, thereby decreasing waste quantities generated. Use of sodium phosphate for increasing total Cr removal and ISX for increasing Cd and Ni removal can be decided on a case-by-case basis.

4. Low Temperature Sludge Drying

The objective of this task was to evaluate the effectiveness of the J-Mate dryer system in further reducing the moisture content of IWTP sludge. The J-Mate dryer system is a closed-loop, low-temperature drying system. Use of such a system to further dry sludge taken from a filter press or centrifuge has the potential to reduce sludge moisture content from 60 to 65 percent down to 30 percent. Because sludge disposal costs are proportional to the mass of sludge needing disposal, removing additional water decreases disposal costs.

Field testing was conducted on two JWI J-Mate dryer systems, the JWI J-210 unit at Ogden Air Logistics Center (OO-ALC) and the JWI J-203 unit at the Lawrence Berkeley National Laboratory (LBLN). Both systems treated dewatered sludge from an IWTP filter press. The two JWI dryer units were evaluated for sludge drying capability, potential for cross-media pollution, and operation and maintenance cost effectiveness. The field tests showed that the J-Mate dryer was capable of reducing the weight of a sludge containing 21 percent solids by about 10 percent. Results with a sludge with an 87 percent initial moisture content showed an 8 percent moisture content reduction. This performance is considered marginal, although the test

sludge initial moisture content of 79 to 87 percent was much higher than the typical 60 to 65 percent. The JWI J-Mate sludge dryers were effective at eliminating pollutant emissions to the atmosphere during the drying cycle.

The electric low temperature sludge dryers may be an economical method of dewatering the IWTP sludge cake, and thus reducing the volume and cost of hazardous waste disposal. Further testing is recommended on more typical dewatered sludge, as the results of these tests on atypical (very high initial moisture content) sludge were less than encouraging.

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ABBREVIATIONS, ACRONYMS AND SYMBOLS

AF-ALC	Air Force-Air Logistic Centers
ASTM	American Society for Testing of Materials
APHA	American Public Health Association
A-LIX	Anion-LIX
atm	atmosphere
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
Cr ^{III} , Cr ³⁺	Chromium with charge of 3+; also Chromium(III)
Cr ^{VI} , Cr ⁶⁺	Chromium with charge of 6+; also Chromium(VI)
DRMO	Defense Reutilization and Marketing Office
E/A or V _E /V _{aq}	Organic solvent (or extractant phase) to aqueous phase volume ratio
E _M	Percent extraction of metal M
EM	Environmental Management
EPA	Environmental Protection Agency
FOG	Fat, oil, and grease
gpm	gallons/per/minute
gpd	gallons per day
ICP or ICAP	Inductively coupled Argon Plasma Elemental Analysis Technique
IWTP	Industrial Waste Water Treatment Plant
LBNL	Lawrence Berkeley National Laboratory
LIX	Liquid Ion Exchange
[M] _A	Concentration of metal M in aqueous phase
[M] _E	Concentration of metal M in extractant phase
MOS	Mixing/Oil Skimming
M-T	McCabe-Thiele Plot
MOS-LLX	Mixing/Oil Skimming Liquid Liquid Extraction
NPDES	National Pollutant Discharge Elimination System
OC-ALC	Oklahoma City Air Logistics Center
OO-ALC	Ogden Air Logistics Center
overbar	Chemical species dissolved in extractant phase (LIX), e.g.,
q	Distribution coefficient in LIX processing,
RCRA	Resource Conservation and Recovery Act
SA-ALC	San Antonio Air Logistics Center
SCC	Solids Contact Clarifier
SM-ALC	Sacramento Air Logistics Center
TCLP	Toxicity Characteristic Leachant Procedure
TAD	Tooele Army Depot
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
TSS	Total Suspended Solids
VOC	Volatile Organic Carbon
WR-ALC	Warner Robins Air Logistics Center

SECTION I

INTRODUCTION

The U.S. Air Force (USAF) needs solutions to reduce or eliminate the large volumes of sludges that are produced at USAF industrial wastewater treatment plants (IWTP). The sludges can contain varying quantities of hazardous materials, such as heavy metals, waste oils, and halogenated organic compounds, in a matrix of solids and water. These sludges are currently disposed as hazardous waste. Increasingly stringent environmental legislation and rising disposal costs require that these streams be reduced or eliminated. As an initial step to meet this requirement, technology to minimize the volume and/or the toxicity of these sludges need to be identified and evaluated.

A. OBJECTIVE

The project objectives were to:

- Identify and characterize the problematic IWTP sludges at the AF-ALCs
- Identify current and potential technologies for resource recovery, volume reduction and/or detoxification of these IWTP sludges
- Evaluate suitable technologies through laboratory and pilot-scale testing at an AF-ALC
- Recommend technology prototyping and implementation.

A two-phased approach was planned to meet the above objectives. This report documents the Phase II actions to evaluate candidate technologies in pilot-scale tests at three ALCs.

B. BACKGROUND

The AF-ALCs generate large amounts (300,000 to 1,000,000 gallons per day) of industrial waste water that must be treated on-site to reduce the toxic (RCRA) metals; total suspended solids (TSS); fat, oil and grease (FOG); and other toxic organic contaminants contributing to BOD and COD. This treatment leads to the formation of large quantities of

"F-waste" (e.g., F002, F005, F006) due to the presence of solvent and metal bearing effluents from plating and metal finishing operations. Such wastes are classified as hazardous because of the "derived from" regulations and therefore carry expensive disposal costs.

In general the AF-ALC's produce three types of IWTP sludges: metal hydroxide sludge, biotreatment sludge and oily sludge. Each sludge has some organic content (BOD/COD) and total suspended solids (TSS) with water still the dominant constituent. These sludges are sometimes mixed for disposal. The needs survey (Task 1.1) and sludge characterization tasks (Task 1.4), described below, quantified each sludge and the composition range for each AF-ALC.

C. APPROACH

The two-phased approach established seven tasks in Phase I to identify the sludge treatment/recycle needs at AF-ALCs and to evaluate and test candidate technologies on a laboratory scale. Available data were collected from each of the five AF-ALCs to establish the quantity, composition, associated disposal cost and source of the IWTP sludges. Additional samples were collected and analyzed to characterize the sludges. A literature review and technology selection effort identified potential technologies for each need. The technologies were ranked using a multiple attribute analysis based on technical and economic criteria. Laboratory testing established the potential waste reduction and cost savings that could be achieved with the candidate technologies and sludge streams. The Phase I results are described in the previous project report dated November 18, 1996. These tests were used to further establish the recommended technologies and sites for pilot testing during Phase II.

This report summarizes field testing (Phase II) of four technologies at three ALCs. Topical reports on each technology/test provide complete details. These technologies and pilot plant test locations are:

- Flocculation/Filtration at Warner Robins ALC
- Chromium/Metal Removal by LIX at Warner Robins ALC
- Alternative Precipitation Chemistry at Oklahoma City ALC
- Low Temperature Sludge Drying at Ogden ALC.

SECTION II

SLUDGE FLOCCULATION AND FILTRATION PILOT PLANT TESTS AT WARNER ROBINS (WR-ALC)

A. INTRODUCTION

The current IWTP plant operations are shown in Figures 1 and 2. Wastewater from the Robins AFB plating shop is sent to the IWTP No. 2. The acids are neutralized and hexavalent chromium (Cr^{VI}) is reduced with ferrous sulfate. The treated wastewater is sent to a clarifier. The rest of the industrial wastes are directed to IWTP No. 1 for Cr^{VI} reduction, metal precipitation, oil-water separation, and settling of suspended solids. Complete characterization data on the waste streams shown in Figures 1 and 2 are given in Section IV.D.2 of the Phase I report for this project.

The settled solids from the IWTP No. 2 clarifier are pumped to the IWTP No. 1 sludge thickener. The combined sludge underflow from this thickener is pumped to a holding tank (decanter) in Building 352. The thickener underflow typically contains about 3.5 percent solids. After settling in the holding tank in Building 352 for 24 to 48 hours, the solids content is increased to around 5 percent. Currently, these settled solids are pumped to a 12,000 gallon mixing tank and mixed with lime to bring the sludge concentration to around 7 percent solids. This sludge is currently pumped at 270 psi pressure to a 20-year old Eimco filter press containing 48 cast iron plates (4 ft-square each) for dewatering. The press is old, difficult to maintain, and inefficient. De-watered cakes are typically 31 to 32 percent solids. The dewatered cake is loaded into 1-ton sacks and sent offsite for disposal at \$0.22/lb.

Current estimated sludge production is 584 ton/year. The elimination of the lime would reduce sludge production by about 92 tons, or a 16 percent reduction in the quantity of sludge needing disposal. Bench-scale testing indicated one of several organic flocculants could be added to either IWTP No. 1, 2, or the combined 1 and 2 sludge stream to allow them to be rapidly and efficiently dewatered without lime addition. The potential savings due to reduced sludge production, the age of the existing press, and IWTP modifications provide ample incentive for investigating alternative dewatering procedures and equipment.

Modifications now underway at the IWTP include separation of the sludge streams from the two IWTPs. A new biological treatment plant is under construction to treat the clarified

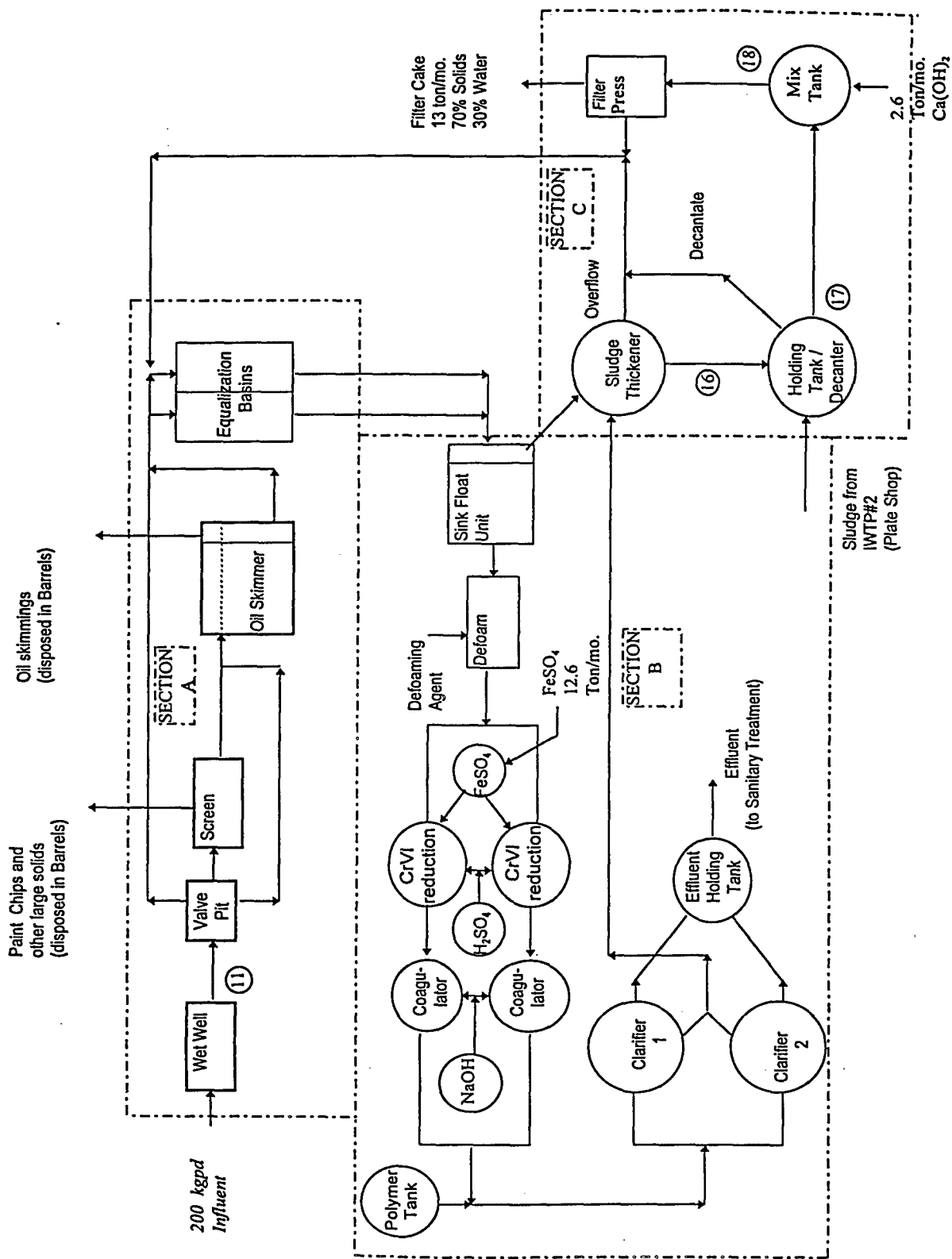


Figure 1. Warner Robins Industrial Wastewater Treatment Plant.

Plating Shop Waste

80,000 gal/day

Divided among the streams 22 and 21

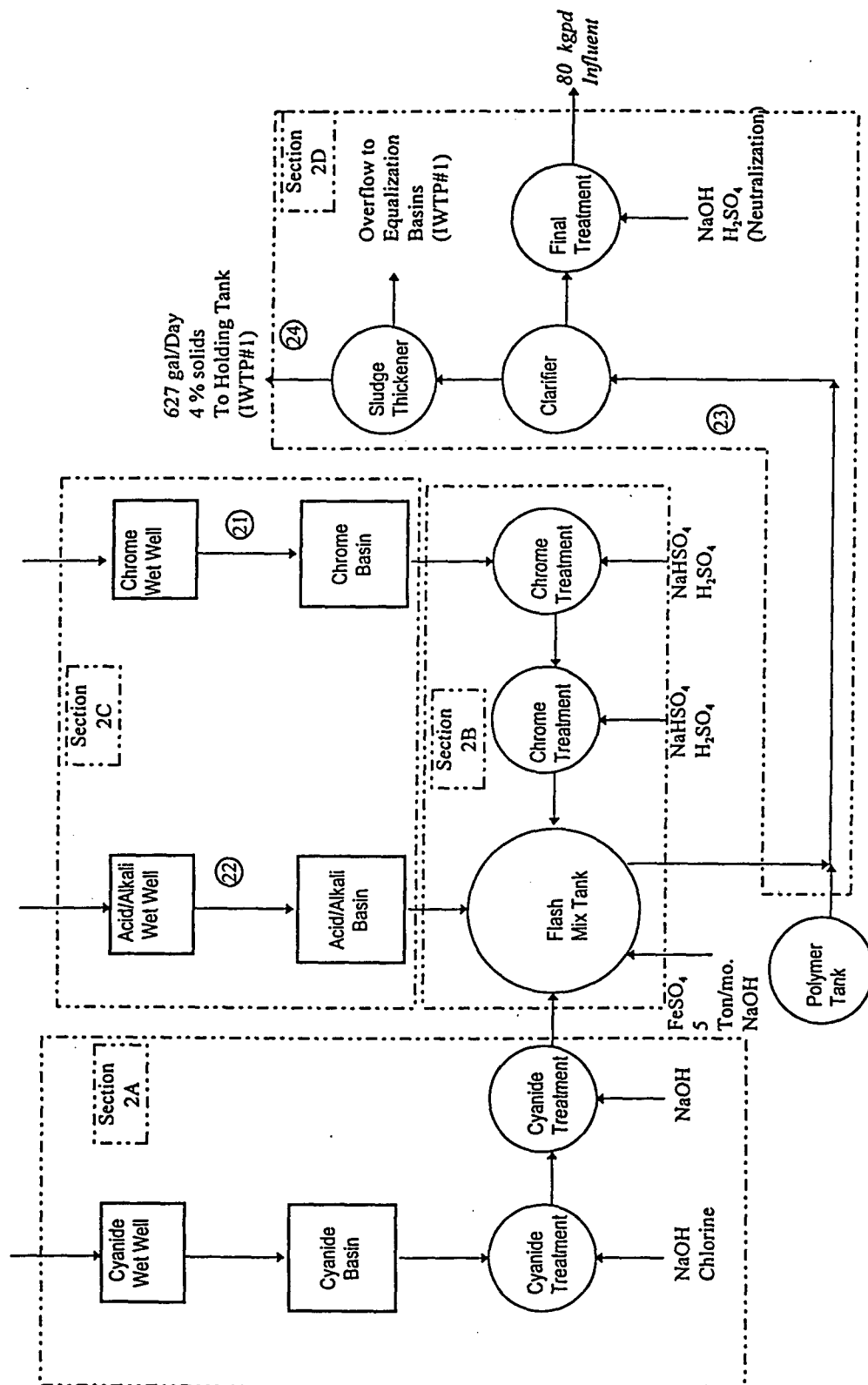


Figure 2. Process Flow Diagram for Warner Robins AFB (WR-ALC) IWTP 2.

water from IWTP No. 1. The sludge from the IWTP No. 1 thickener and sludge produced in the new biological treatment plant will be pumped to the existing filter press. The sludge from IWTP No. 2 will be directed to a new facility housing a flocculant addition system and a new JWI filter press. In addition, replacement of the existing filter press is being actively considered.

B. OBJECTIVES

The field test objectives were to:

1. Demonstrate on a pilot-scale basis that IWTP sludges produced at Warner Robins AFB could be effectively dewatered without the use of lime
2. Determine the dewatered cake solids content and the filtrate characteristics (percent suspended and dissolved solids)
3. Quantify the amount and type of flocculant required for effective dewatering
4. Estimate the economic benefits of eliminating lime addition to the sludge dewatering operations.

C. TEST PLAN

During June 1996, the first series of the experimental test program was conducted. The focus during series 1 was the sludge from IWTP Plant No. 2 which will be processed separate from IWTP Plant No. 1 sludge after the current plant upgrades are in place. Series 2, conducted in July, focused on the combined IWTP No. 1 and 2 sludge, i.e., IWTP stream # 17 which is the only sludge being processed today after mixing lime with it. Each series included evaluation of flocculant type, dosage, sludge feed pressure, and/or cloth permeability. Also, in series 1, the effect of using high-pressure gas and special filter membrane plates to remove additional water from the cakes was evaluated.

1. Experimental Apparatus

The experimental setup included the following equipment items:

- 1000 gal sludge holding tank, with recirculation pump

- 30-gal sludge-flocculation mixing tank (it also served as the flocculant preparation tank) with mechanical agitator
- 470-mm (1.5 ft by 1.5 ft wide plates) JWI filter press. The press included 3 effective plates, either standard 32-mm (cake thickness) plates or 25-mm membrane plates. The three plates provided two cake formation chambers. Also two sets of polypropylene filter cloths were available for testing, the first with a permeability of 4 cfm/ft² and the latter with 25 cfm/ft²
- Air diaphragm pump (two separate pumps, one for 100-psi and one for 200-psi feed pressure testing),
- Electronic scale, to measure the weight of the mixing tank and contents, and
- Moisture balance for rapid determination of slurry and sludge solids content.

The photographs of the test facility are shown in Figures 3 and 4.

2. Experimental Procedure

The experimental procedure included the following steps:

- Fill the 1000 gal tank with approximately 900 gal of sludge withdrawn from the bottom of the IWTP No. 2 clarifier or the IWTP No. 1 thickener (which contained the combined sludge from IWTP No. 1 and 2)
- Determine the sludge feed solids content
- Calculate the required quantity of flocculant
- Prepare a concentrated stock solution of the flocculant under study
- Dilute the flocculant stock solution to 500 to 1000 ppm while preparing approximately 20 gallons of flocculant solution
- Attach the desired filter cloths to the selected filter plates; insert the plates into the filter assembly; and use the hydraulic ram to pressurize the plates to 4100 psi
- Recirculate the IWTP sludge in the 1000 gal tank for 10 minutes; turn off the mixing-tank agitator; then transfer approximately 20-gal of sludge from the 1000-gal tank to the mixing tank



Figure 3. Photograph of the Test Facility Showing the 1000-Gallon Sludge Holding Tank.

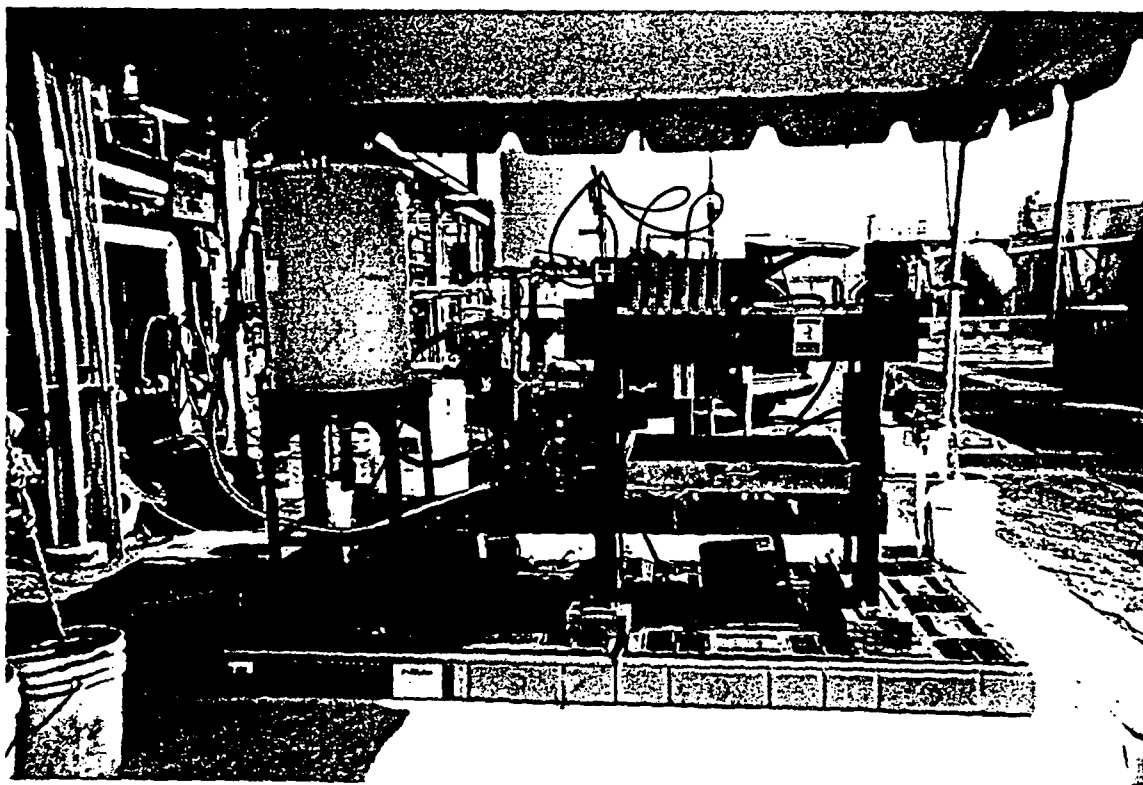


Figure 4. Photograph Showing the Sludge Dewatering Pilot Plant Facility.

- Turn on the mixing-tank agitator; agitate for 30 sec at a high rate to flocculate sludge, reduce agitation rate to keep solution dispersed but avoid floc breakup. (In some experiments, decantation of excess water was employed by stopping the agitation for some time, and then the thickened sludge was remixed.)
- Regulate the air pressure to the selected air-diaphragm slurry feed pump; pump at 25 psi and begin slurry feed to the filter press
- Record mix tank weight (to measure solution feed rate) every minute for the first 10 minutes, then every 5 minutes thereafter; calculate filtration rate
- Continue operation until the filtrate rate drops below approximately 0.01 gal/min per ft² (approximately 260 ml/min for the 470-mm filter press)
- Increase rate to 50 psi and continue filtering until the filtration rate drops to near the 260 ml/min cutoff rate; repeat for 75 psi and 100 psi (note: in testing with the high pressure slurry feed pump, air pressures of 25, 50, 75, and 100 psi translated into slurry feed pressures of approximately 50, 100, 150 and 200 psi)
- After the filtration rate drops below the cutoff rate, stop the feed pump. Use 40 psi air to blow water from the filtrate collection lines
- When conducting a pressure squeeze, attach a gas line from a nitrogen cylinder to the membrane filter; increase the nitrogen pressure to 50 psi, and hold until the filtration rate dropped below the 260 ml/min level. Repeat the process at regulated nitrogen pressures of 100, 150, and 225 psi. Hold the unit for 5 minutes at the 225 psi level before relieving the squeeze pressure
- Release the hydraulic-ram pressure which is used to keep the plates in place; open the filter press and remove the dewatered filter cakes
- Determine the cake weight and take samples for solids content determination
- Determine overall weight of filtrate collected and take sample for turbidity analysis.

3. Results and Discussion

Two test series were conducted. In the first series, IWTP No. 2 sludge was dewatered after flocculation with Cytec 1820 A, an anionic emulsion flocculant. In series 2, the combined IWTP No. 1 and 2 sludge (IWTP stream # 17) was flocculated with either Percol 727 (an anionic solid flocculant) or Nalco 7768 (an anionic emulsion flocculant). In both cases, the sludge was readily dewatered. The flocculated sludge was fed into the press to produce a low solids filtrate and a firm, high-solids filter cake. The dewatered cakes were easily handled and no evidence of cloth blinding was observed.

a. Results for IWTP No. 2 Sludge. The test results indicate that the IWTP No. 2 sludge can be readily dewatered using a JWI filter press. Preconditioning with lime was not necessary to obtain high cake solids contents, rapid dewatering, and the production of clear filtrates. The use of 10 to 15 lb/ton dry solids of a flocculant (Cytec 1820A) allowed a 1 to 2 percentage point improvement in cake solids content over non-flocculated sludge.

A photograph of the dewatered IWTP No. 2 sludge, as discharged from the press, is shown in Figure 5. The clear impression of the filter cloth texture demonstrates the lack of filter fouling and easy discharging of the filter cake. The test conditions and results are summarized in Table 1.

The test results indicate that raw or flocculated IWTP No. 2 sludge can be easily handled and rapidly dewatered to produce high solids filter cakes and clear filtrates. Lime addition can be eliminated. After filtration, the filter cakes were readily released from the filter cloths providing for easy filter operation. There was no evidence of filter cloth blinding, so low maintenance press operation can be anticipated. Optimal performance was obtained when operating at 180 psi final feed pressure using Cytec 1820A flocculant at a dosage of 15 lb/ton dry solids.

b. Results for Combined IWTP Nos. 1 and 2 Sludge. The test results indicate that the combined IWTP No. 1 and 2 (IWTP stream # 17) sludge can be readily dewatered using a JWI filter press. Preconditioning with lime was not necessary to obtain high cake solids contents, rapid dewatering, and the production of clear filtrates. The use of 3 to 4 lb/ton dry solids of Percol 727 (an anionic powder flocculant) or 14 to 18 lb/ton dry solids of Nalco 7768 (an anionic emulsion flocculant) allowed a 6 to 7 percentage point improvement in cake solids content.

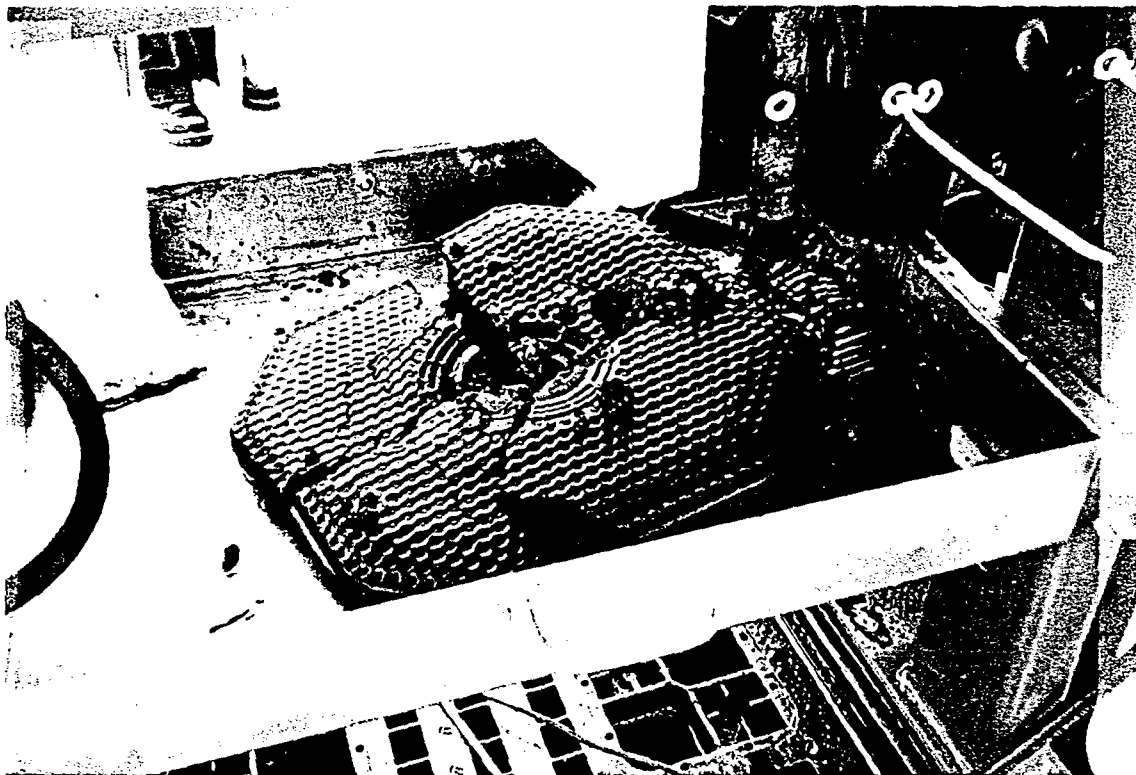


Figure 5. Photograph of Dewatered IWTP No. 2 Sludge.

**TABLE 1. IWTP NO. 2 SLUDGE DEWATERING TEST CONDITIONS AND RESULTS.
(TOTAL FILTER CAKE PRODUCED ≈ 250 lb)**

Run No.	Test Conditions					Test Results			
	Cloth Permeability (cfm/ft ²)	Polymer Dosage (lb/ton DS)	Maximum Slurry Feed Pressure (psi)	Feed Solid Content (%)	Cake Thickness (mm)	Filtration Time (min)	Cake Solids Content (%)	Filtrate TDS (ppm)	Filtrate TSS (ppm)
1	4	15	100	6.9	25	103	29.1	324	2
2	4	13.5	100	6.9	25	110	30.8	377	1
3	4	10	100	6.3	32	125	29.0	329	16
4	4	13.5	140 ^(a)	6.3	32	115	28.5	351	17
5	4	0	170 ^(a)	6.3	32	60	28.3	552	0
6	4	15	150 ^(a)	6.3	32	110	31.5	353	61
7	4	15	100	6.6	25	130	29.8 ^(b)	350	4
8	25	15	100	6.6	25	125	35.3 ^(b)	363	17
9	4	0	100	6.0	25	60	27.0 ^(c)	632	85

(a) Maximum pressure obtainable due to limited compressed air supply

(b) These tests employed a post-dewatering "pressure squeeze." It is estimated that squeezing increased the percent solids level by 3 to 5 percent

(c) Repeat test conducted during second test period.

The test conditions and results are summarized in Table 2. All the filtrations but one proceeded smoothly. The exception was a breach of the filter cloth during the first Nalco pressure filtration. Much sludge was found behind the filter cloth but the exact location of the leak in the filter that breached was not found. There was, however some indication of creases that may have been related to the breach.

The sludge solids content was varied from 5.5 percent on the first day to 5.1 percent on the last day. The reason for the lower solids content of the sludge is related to the settling of the heavier solids in a portion of the tank not mixed by the circulation of the sludge. At the end of the experiments, the sludge residue at the bottom of the tank was concentrated on the far wall from the circulating stream as shown in Figure 6. The sludge was different from the previous samples; the sludge retained its black color although it was exposed to air over a day. The fuel and septic odor and the oil layer floating on top of the filtrate distinguished this sludge from the previous samples.

During dewatering, some sludge passed through the filter cloth when flocculated with low flocculant dosage or without flocculant at all. The filters were not blinded when running flocculated or non-flocculated sludges.

The filter cakes had high solids content at the external layers and at the edge of the cake, however the solids content was lower than achieved in the laboratory filtrations. Samples of dewatered cake were withdrawn from different locations on the filter cake (see Figure 7). The core had up to 7 percentage point lower solids content than the average, and the edge had 1 to 6 percentage point higher percent solids.

TABLE 2. IWTP NO. 1 AND 2 SLUDGE DEWATERING TEST CONDITIONS AND RESULTS^(a).

Run No.	Test Conditions					Test Results			
	Flocculant Type	Flocculant dosage (lb/ton DS)	Maximum Slurry Feed Pressure (psi)	Feed Content ^(b) (%)	Cake Thickness (mm)	Filtration Time (min)	Composite Cake Solids Content ^(c) (%)	Filtrate TDS (ppm)	Filtrate TSS (ppm)
11	Percol 727	3.6	100	3.4	25	115	25.0	634	366
12	Percol 727	3.6	186	3.4	25	85	27.5	680	2100
13	Nalco 7768	16	150 ^(d)	3.4	25	65	29.9	520	1350
14	Nalco 7768	16	180	3.4	25	115	26.2	576	288
15	Percol 727	3.2	180	3.4	25	95	28.9	540	400
16	None	0	180	3.4	25	110	23.8	520	1150
17	Percol 727	4	180	3.4	25	110	28.3	548	460
18 ^(b)	Nalco 7768	14	180	4.7	25	95	32.7	540	860
19 ^(b)	Nalco 7768	18	180	4.7	25	95	31.3	480	1260
20 ^(b)	Percol 727	3.6	180	4.7	25	95	28.5	456	380

(a) Cloth permeability for all tests: 25 cfm/ft²

(b) Runs 18-20 used sludge, which was decanted to a solids content of 4.5 to 4.8 percent. The previous runs (non-decanted) had a solids content of 3.2 to 3.5 percent solids. The sludge is diluted during flocculation by addition of the dilute flocculant in proportions of 4 parts flocculant solution to 7 parts sludge

(c) Composite value obtained from a weighted average of the percent solids determined from samples taken from the core (22 percent), external layer (22 percent), and edge (56 percent). The core had up to 7 percentage point lower solids content than the average and the edge had 1 to 6 percentage point higher percent solids levels

(d) The filter cloth was "breached" in this run allowing sludge to pass behind the cloth and partially by-pass the filter cloth.

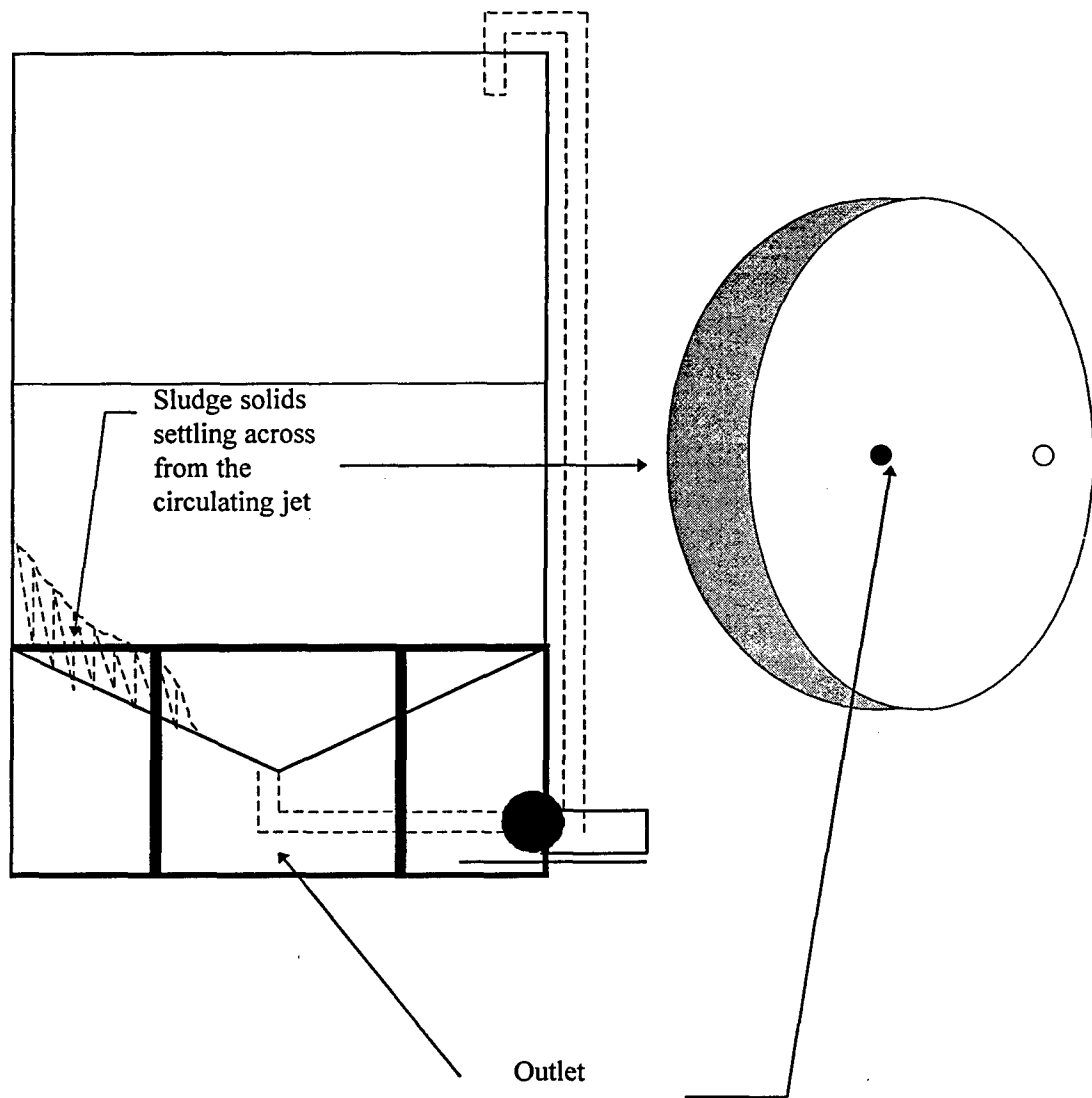


Figure 6. Solids Deposition in the Holding Tank.

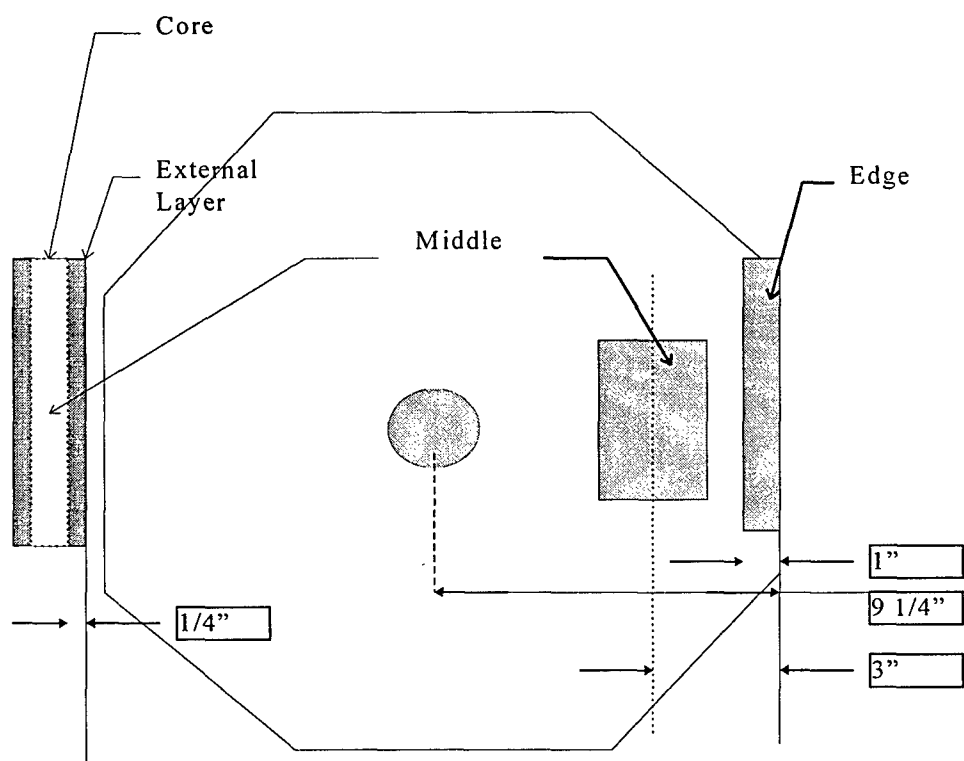


Figure 7. Sampling of Cake for Solids Content (not to scale).

The following observations were made:

1. Maximum pressure: 100 psi compared to 180 psi. The high-pressure filtration was shorter by 30 minutes under the same run conditions. The high pressure filter cake had a softer core (21 percent compared to 26 percent) but had a much denser edge area containing 34 percent solids compared to 26 percent in the edge of the cake obtained at the lower pressure.
2. Polymer type: Nalco 7768 vs. Percol 727. The composite results of the pressure filtrations of sludge flocculated with both polymers showed a better solids content in the cake core and edge using Nalco 7768. The difference was more pronounced in the runs performed with decanted flocculated sludge where the Nalco polymer had a solids content of 32 percent (average for both runs) compared to 28.5 percent for the Percol polymer.
3. Decantation of flocculated sludge: decanted vs. non-decanted. Decantation was beneficial, resulting in an improvement in the solids content of the filter cake core from 24 percent \pm 3 percent to 29 \pm 3 percent. Cake core solids content for Percol 727 flocculant at 3.6 lb/ton dry solids was improved from 21 percent to 26 percent solids. Most significant was the firmness of the cake core obtained by pressure filtration following decantation which is a great improvement over the liquid and semi-liquid cores obtained without it. The handling characteristics of the cakes were improved in this way.
4. Polymer loading effects. Polymer loadings were tested within + and - 10 percent of the recommended loading previously determined in the laboratory experiments and modified according to the initial jar tests conducted in the field.
 - a. Percol 727 performance was roughly consistent at the loadings 3.2, 3.6 or 4 lb per ton dry solids. The difference in the filter cake core solids content among the 3 Percol runs (without decantation, at 180 psi) is attributable to the shorter filtration time of Run 12. Percol 727 jar tests showed little effect of loadings beyond 3.2 lb per ton dry solids, however, sludges treated with loadings below 3.2 were not fully flocculated

- b. Nalco 7768 performed well at loadings of 14 to 18 lb per ton dry solids. This is consistent with the results of the jar tests, in which complete flocculation was achieved with loadings of 14 lb per ton dry solids and "buckshot" flocs were created at loadings of 16 and 18 lb per ton dry solids. Runs of decanted flocculated sludge at both 14 and 18 lb per ton dry solids gave high solids content of about 32 percent.

The test results indicate that raw or flocculated combined IWTP No. 1 and 2 sludge can be easily handled and rapidly dewatered to produce high solids filter cakes and clear filtrates. Lime addition can be eliminated. After filtration, the filter cakes readily released from the filter cloths providing for easy filter operation. There was no evidence of filter cloth blinding, so low maintenance press operation can be anticipated. Optimal performance was obtained with more concentrated feed slurries (i.e., decanted), operated at 180 psi final feed pressure using Nalco 7768 flocculant at a dosage of 18 lb/ton dry solids.

D. ECONOMIC ANALYSIS

The use of lime at the IWTP operations at Robins AFB (WR-ALC) can be curtailed or eliminated entirely by the use of flocculants for the treatment of some of the sludges. Furthermore, the waste sludge volume can be reduced by using the flocculants tested in this program compared to sludge volume obtained by the use of lime.

The best dewatering performance on sludge IWTP#17 from WR-ALC was obtained with Nalco 7768 at loadings above 18 lbs/ton dry-solid and is relatively insensitive to loadings above that level. The upgrade program for the IWTP at WR-ALC includes the installation of a new filter press for the separate filtration of IWTP No. 2 sludge that is produced by the plating shop waste water treatment plant (IWTP No. 2). IWTP No. 2 sludge is currently mixed with the Plant 1 sludge and thickened to form IWTP stream No. 17. The IWTP No. 2 sludge may be flocculated easily using Cytec 1820 at loadings of 15 tons dry solid, respectively. The solids content that has been obtained by pressure filtration at 180 psi following flocculation is approximately 31 percent solids.

The waste volume reductions that may be obtained by the use of flocculants in treating WR-ALC sludges are summarized in Table 3. Simplified block process flow diagrams for the WR-ALC IWTP before and after implementing the proposed process are shown in Figures 8 and 9, respectively. The estimated sludge volume reduction for a 180 psi press is expected to be about 16 percent. The proposed process will require the equipment changes shown in Figure 10. The addition of a flocculation system is shown by dotted lines in Figure 10.

An estimate of the economic potential of the proposed dewatering options was made for the WR-ALC sludges. The procedure for economic analysis was as follows:

- (1) The purchased equipment cost (PEC) of equipment to be purchased was estimated using standard cost estimation procedures¹
- (2) The installed equipment cost was estimated by applying a factor to PEC¹.
- (3) The incremental chemical, labor, and utility costs were estimated.
- (4) The costs for maintenance, supervision, laboratory use, and plant overheads were taken as fixed percentages of the labor cost.
- (5) Based on the net cost savings from a reduction in quantity of sludge disposed and an increase in operating cost for new equipment, a simple paycheck calculation was made.

The cost of labor involved in operating the flocculation system is estimated to be the same for lime treatment of sludge. A summary of the economic analysis is given in Table 4. The sludge quantity can be reduced by 16 percent (i.e., by 92 tons/yr) with a net annual savings of \$32,000. The simple payback period is estimated to be 2.0 years. Moreover, since lime addition is a manual operation, the proposed process is expected to be more acceptable to the IWTP operators.

This cost estimate assumes that the equipment for polymer preparation and polymer-sludge mixing is currently unavailable for the combined sludge from the two IWTP plants. In reality, the IWTP No. 2 plant is currently being renovated and has a polymer mixing/addition system under procurement. So, only the system for handling the remainder of the sludge needs to be procured.

¹ Peters, M.S. and Timmerhaus, K.D., "Plant Design and Economics for Chemical Engineers," 4th Edition, McGraw-Hill Chemical Engineering Series, ISBN 0-07-049613-7, 1991.

TABLE 3. WASTE VOLUME REDUCTION BY PRESSURE FILTRATION OF FLOCCULATED WR-ALC SLUDGES IWTP 17 AND IWTP 2 (BASIS: 100 lb OF THICKENED SLUDGE AT 5 PERCENT SOLIDS).

	Current Treatment of IWTP#17 Filtered at 270 psi 90 min	Separation of IWTP#2, Filtered at 180 psi 95 min	Flocculation of IWTP#17 Filtered at 150 psi 110 min
Solids content	31.4%	31%	31%
Additive	Lime	Cytec 1820A flocculant	Nalco 7768 flocculant
Dosage, lb/ton dry solid	400	15	18
Additive quantity added, lbs	1	0.0375	0.045
Final waste, quantity, lbs	19.1	16.1	16.1
Waste reduction compared to current treatment, %	NA	16%	16%

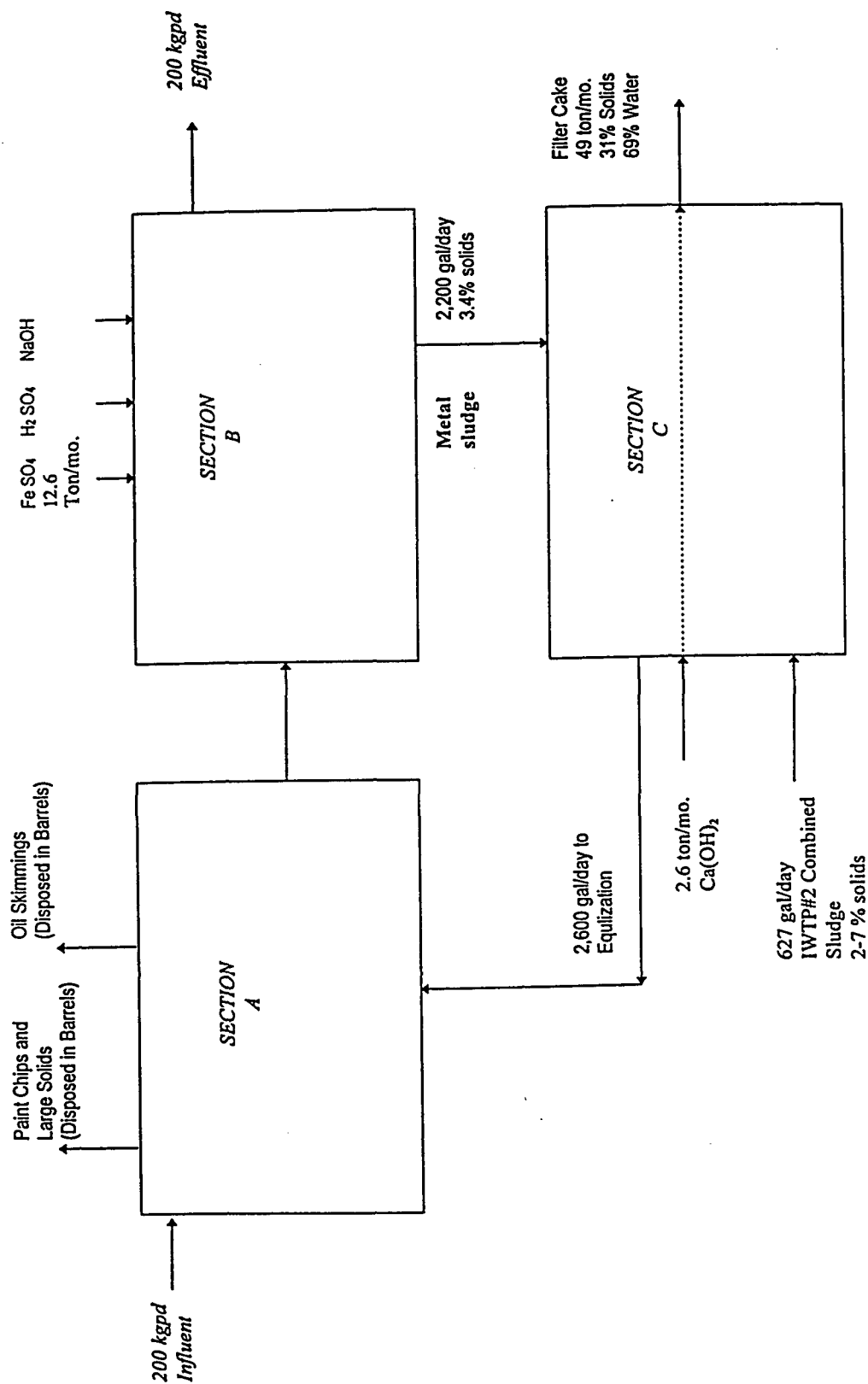


Figure 8. Block Process Flow Diagram of WR-ALC IWTP Plant.

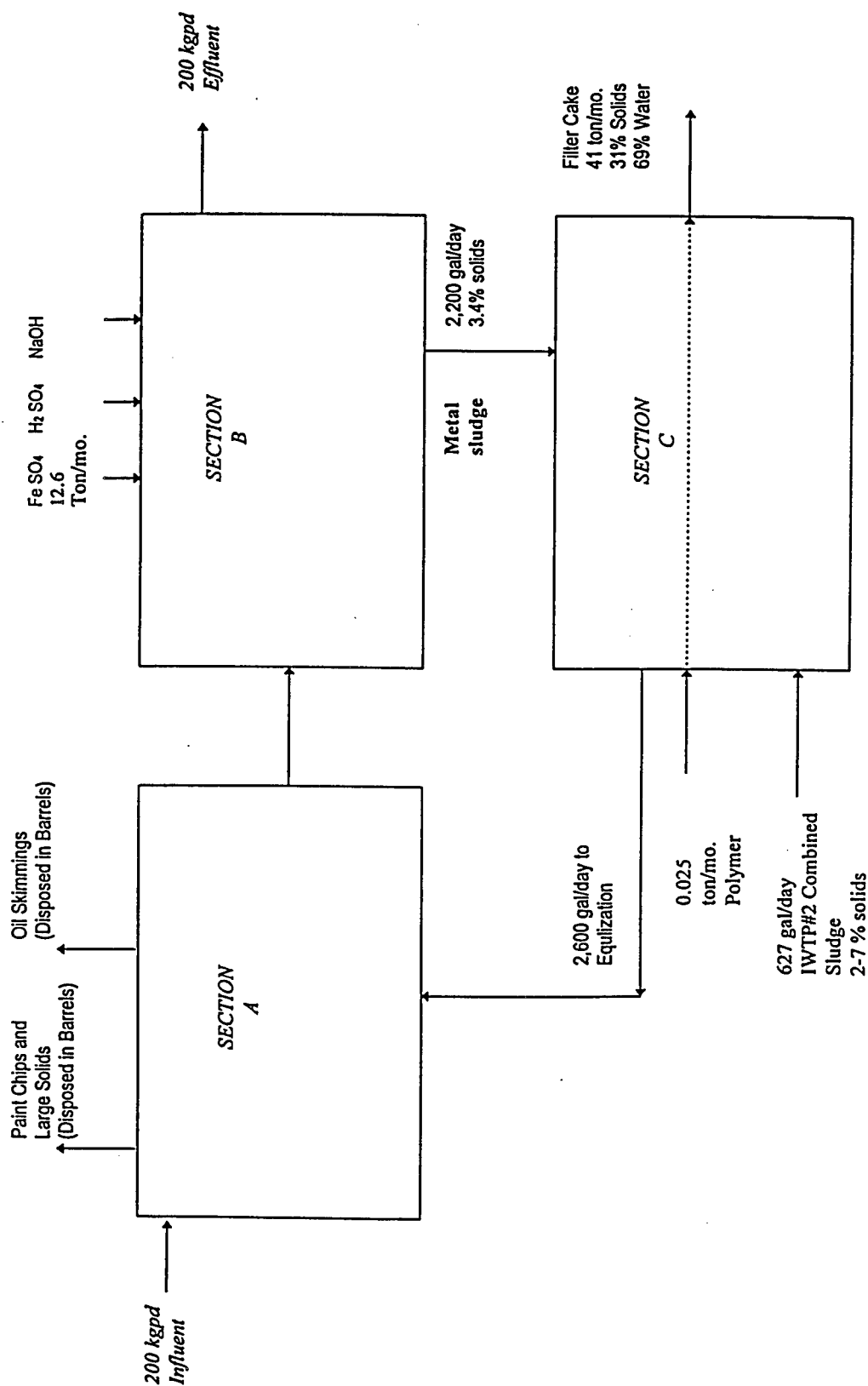


Figure 9. Effect of Proposed Flocculation Process on Process and Waste Streams at WR-ALC IWTP (Plant No. 1).

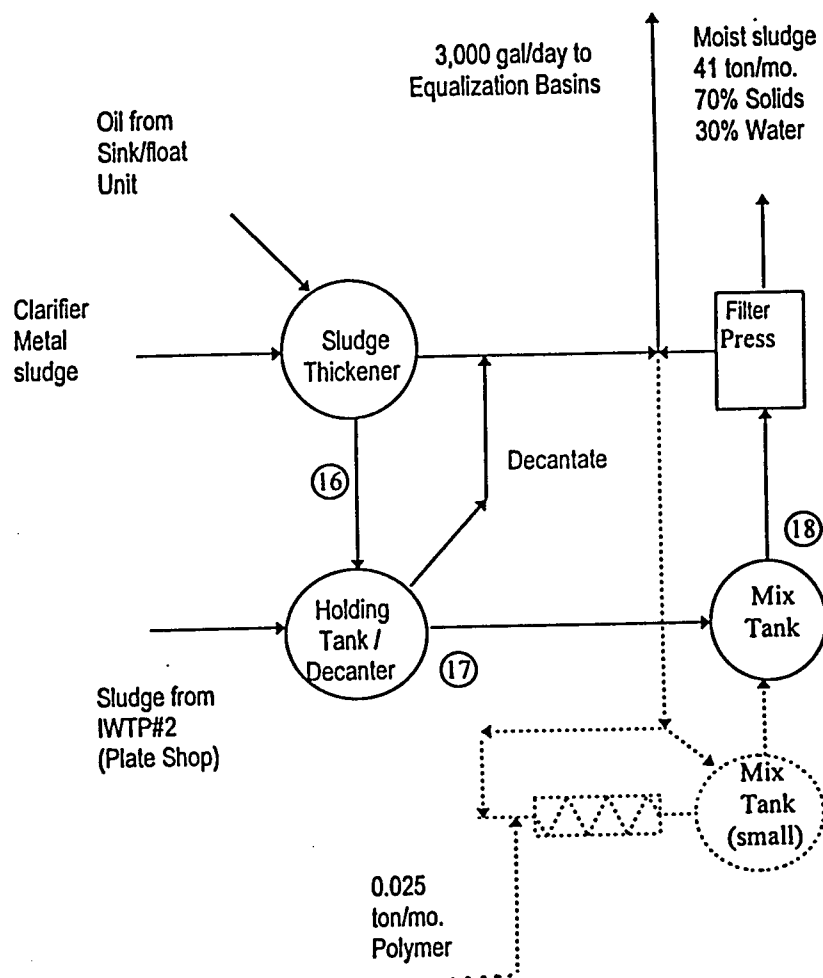


Figure 10. Proposed Equipment Changes for Flocculation of Combined Metal Sludges (IWTP 17).

**TABLE 4. ECONOMIC ANALYSIS OF PROPOSED FLOCCULATION/DENSITIES
PROCESS FOR WR-ALC IWTP 17 SLUDGE.**

Treatment Method,	Cr reduction	Current
	Metal removal	Current
	Sludge treatment	Flocculation
Operating Schedule	Hrs/year 1,920	Electricity, cent/kWh 3.785
Hrs/shift 8	Shifts/day 1	Waste disposal cost, \$/lb 0.22
Days/week 5	Reduction of Sludge Quantity 92 ton/year	
Weeks/year 48	for Disposal 16 Percent	
PLANT CAPACITY	Flow rate, gal/day	280,000
CAPITAL COST		
Purchased Equipment Cost (PEC)		\$ 23,000
	Basis	Percentage
Installation	PEC	40%
Instrumentation	PEC	20%
Piping	PEC	25%
Electrical	PEC	15%
Engineering	PEC	30%
Contingency	PEC	50%
Fixed Capital Investment (FCI) \$ (1996, installed)		\$ 64,400
OPERATING COST, \$/yr		
	Basis	Percentage
Materials		\$ 1,831
Maintenance,	FCI	6%
Operating Supplies	maintenance	15%
Electricity		
Operating labor		Current
Supervision,	labor	Current
Laboratory charges,	labor	Current
Plant overhead costs	Supervision+labor +maintenance	60%
		\$ 2,318
Total operating cost		\$ 8,593
COST SAVINGS, \$/yr		
Savings in waste disposal cost		\$ 40,338
Net cost savings		\$ 31,745
PAYBACK PERIOD, yr		2.0

E. CONCLUSIONS

Several conclusions were drawn based on the test results and observations made during the test series. These are noted below:

- IWTP No. 2 sludge, and the combined IWTP No. 1 and 2 sludge (IWTP stream # 17), can be readily dewatered using a JWI filter press. So, the proposed flocculation process can be immediately implemented to dewater the mixed sludge with a new filter press. Later on, when the two sludges are segregated, they can be separately flocculated and pressed.
- Preconditioning with lime was not necessary to obtain high cake solids contents, rapid dewatering, and the production of clear filtrates.
- 10 to 15 lb/ton dry solids of an anionic, emulsion-type flocculant (Cytec 1820A) allowed a 1 to 2 percent improvement in cake solids content of unflocculated IWTP No. 2 sludge. A 6 to 7 percentage point improvement in cake solids content was obtained with 16 to 18 lb/ton dry solids of an anionic, emulsion-type flocculant (Nalco 7768) added to unflocculated combined IWTP No. 1 and 2 sludge.
- Increased slurry feed pressure, over the 100 to 170 psi ranges tested, appeared to reduce required filtration time and increase cake solids content.
- Higher permeability filter cloth allowed a slight improvement in cake solids content. However, the higher permeability cloth did produce a significantly dirtier filtrate during the first several minutes of the cake dewatering cycle, and overall a higher turbidity filtrate.
- Cake thickness did not have a significant impact on filtration time, cake solids content, or filtrate clarity.
- Post-dewatering pressure squeeze produced 3 to 5 percentage point dryer filter cakes. However, economic analysis indicates the savings are not sufficient to justify the extra capital and operating costs associated with membrane plates required for pressure squeeze filtration.

F. RECOMMENDATIONS

1. For Robins AFB

1. Operate the new JWI filter press for the dewatering the IWTP No. 2 sludge with flocculant addition. Eliminate the use of lime. Equip the press with high permeability (e.g. 4 to 25 cfm/ft²) cloth. Evaluate both no flocculant operations and the use of Cytac 1820A at a dosage of 10 to 20 lb flocculant/ton dry solids for improved dewatering.
2. Purchase a new filter press for dewatering the combined IWTP No. 1 and biological treatment sludge stream. Select a filter press capable of operating at 200 psi and equip the press with high permeability (e.g. 4 to 25 cfm/ft²) cloth. Include a system for flocculant addition. (Such a system for IWTP No. 2 plant is apparently already in procurement.) Consider addition of a thickener or holding tank up front of the press so the sludge fed to the filter can be as concentrated as possible. Evaluate the use of Nalco 7768 at a dosage of 10 to 20 lb flocculant/ton dry solids for improved dewatering.
3. Do not retrofit the existing filter press for the use of flocculants.

2. Other Air Force Bases

1. Consider the use of flocculants to eliminate the use of lime in the dewatering of metal- precipitant and industrial wastewater-treatment sludges. Select a filter press capable of high-pressure (i.e, 200 psi) operation. Do not select the pressure squeeze option, as it is not cost effective for these types of sludges.
2. Sludge-specific tests should be conducted to identify the best types of flocculants and the preferred dosages.

SECTION III

CHROMIUM REMOVAL BY ANION LIQUID ION EXCHANGE AND METAL REMOVAL BY MIXED OIL SKIMMING

A. OBJECTIVE

The field test objective was to demonstrate at a pilot scale the application of two liquid-liquid extraction (LLX) technologies, A-LIX and MOS, in removing toxic heavy metals from industrial wastewater streams. The specific objectives for the project were to:

- Establish reaction rates and equilibrium data for the extraction and stripping of heavy metals, primarily hexavalent and trivalent chromium (Cr^{VI} and Cr^{III}), from aqueous wastewater streams using A-LIX and MOS extractants.
- Configure the pilot scale liquid extraction system for A-LIX and MOS field trials based on the above findings, and determine the best MOS extractant for the field trials.
- Test the capability of continuous A-LIX and MOS processes for removing toxic heavy metals from IWTPs.
- Collect data for the scale-up to a commercial full-scale unit.

B. BACKGROUND

The use of LLX technologies for the removal of metals from aqueous streams is well established. The A-LIX and MOS process variations allow for not only the removal of trace metals but also the recovery and concentration of the metals into potentially useful products. In the A-LIX process, anionic Cr^{VI} is targeted, and in the MOS process, the cationic metals Cr^{III} , Cd, Cu, and Fe are targeted.

The field trials took place at WR-ALC. IWTP 2 receives about 40,000 gallons per day of wastewater containing approximately 6-ppm Cr^{VI} , less than 1-ppm Cr^{III} and lower concentrations of Cu, and Cd. The source of this aqueous waste stream is WR-ALC's plating shop.

The source of the chromium is the Alodine used in chromium plating, in the production of conversion coatings, and in painting operations. Alodine is an aqueous solution of primarily chromium trioxide, CrO_3 (which forms chromic acid, H_2CrO_4), and a small amount of sulfuric acid. The oxidation state of the chromium in these solutions is hexavalent chromium (Cr^{VI}). The specific chemical species in solution are discussed below.

As used in metal plating, most of the chromium from the Alodine bath ends up on parts as chromium metal, Cr^0 . However, some Cr^{VI} is reduced to Cr^{III} by galvanic reactions occurring while the metal surface is exposed and the initial Cr^0 layer forms. Because the plating cell is undivided, this Cr^{III} is re-oxidized at the anode back to Cr^{VI} , and does not represent a loss of chromium raw material provided the anode surface area is sufficiently larger than the cathode surface area. These baths typically have a very long lifetime, about ten years, with the only wastewater stream being the rinse water containing dilute Cr^{VI} .

In conversion coating large parts and in painting operations, the Alodine solution is applied to the parts and then rinsed off. This diluted rinse is not reusable and represents a discharge stream containing Cr^{VI} , at 1 to 10-ppm (at the sump discharge).

Therefore, from both the plating and the painting/conversion coating operations, the Cr^{VI} waste is a slightly acidic water solution containing 1 to 10-ppm Cr^{VI} . These Cr^{VI} concentrations are above regulated discharge levels. Handling the order of magnitude variation in concentration represents an additional challenge on any process used to remove this Cr^{VI} .

Current operational practice is to treat industrial wastewater using metal hydroxide precipitation with ferrous salts and caustic, creating large amounts of solid waste. The use of A-LIX and MOS technologies would recover the chromium and other metals without creating high volumes of iron containing sludges, and provide the possibility of recycling and/or reusing these metals.

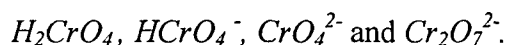
The extractants used in these trials were chosen in Phase I, and are Alamine 336[®] for A-LIX extraction of Cr^{VI} , and NTHA-7 for the MOS extraction of Cr^{III} , Cu and Cd. Information on these water insoluble, liquid extractants is given below:

<u>Extractant</u>	<u>Product type</u>	<u>Manufacturer</u>	<u>Target Metal</u>
<u>Alamine 336®</u>	Tertiary alkyl amine	Henkel-America Corporation	Cr ^{VI}
<u>NTHA-7</u>	Hydroxamic acid	Met Tech Systems	Cr ^{III} , Cu, Cd

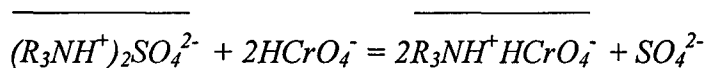
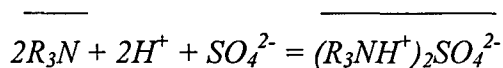
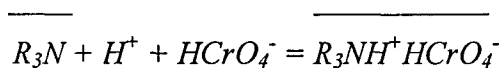
Note that the A-LIX extractant, Alamine 336®, will extract Cr^{VI}, but will not extract the other metals. Likewise, the MOS extractant, NTHA-7, will extract Cr^{III}, Cu and Cd, but is not effective for Cr^{VI}.

1. A-LIX Chemistry

A-LIX is a form of LLX where the extraction mechanism is ion pairing. Cr^{VI} exists in aqueous solutions as anionic species, and oil soluble cationic extractants are effective for the recovery of anions. The species of Cr^{VI} present in water, depending on pH and total Cr^{VI} concentration, are:



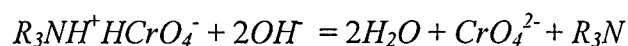
In highly dilute solutions with moderate acidity, the primary Cr^{VI} species is HCrO₄⁻. With sulfuric acid to produce the moderately acidic conditions, the extraction reactions using Alamine 336® are:



where the overstruck species represent the extractant phase. Chromate is exchanged for SO₄²⁻ because of the relative affinities and solvation energies of the two anions. Alamine 336® enters

the process as a neutral species. Only by contacting an acid does it obtain the positive charge needed for the ion pairing to occur. Either sulfuric acid or chromic acid can provide the needed protons.

The stripping of the chromium from the loaded extractant is accomplished by contacting the extractant phase with a base as shown in the following reaction for contact with aqueous sodium hydroxide,

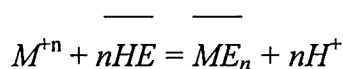


In the stripping reaction the extractant is returned to its neutral state which can no longer ion pair with the hexavalent chromate ion, thereby forcing the chromium into the aqueous phase to maintain charge balance.

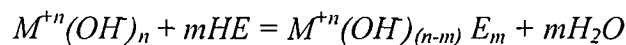
In order to concentrate Cr^{VI} in the strip solution, the net transport of Cr^{VI} must be against its concentration gradient. To accomplish this, a large proton concentration gradient is used to drive the reactions (extraction pH ~4.5, strip pH ~11). The result is the co-transport of chromate ions with protons; first into the extractant phase, and then into the strip solution. This mechanism results in extremely high Cr^{VI} concentration factors.

2. MOS Chemistry

If given sufficient time (up to tens of hours), the chemistry for the extraction of broad spectrum metals from water would be the following:



where M^{+n} represents all metal cations in the IWTP influent, such as Cu^{+2} , Cd^{+2} , and Cr^{+3} . HE represents the water insoluble weak organic acid NTHA-7. This extractant is a metal chelating compound that reversibly binds to metals, making them oil soluble. Mixing/Oil Skimming operates with residence times much shorter than the time needed for the above reactions to occur. Instead, the metal hydroxides are extracted, because they complex with the extractant quickly.



These metal hydroxides are also not as tightly bonded to the extractant as the metal cations, and can therefore be stripped more quickly. The metals are stripped from the extractant by contacting with a strong acid. The fast extraction and stripping rates promise to substantially lower LLX contactor equipment costs by decreasing equipment sizes, especially for Cr^{III}.

3. Approach

The test results were designed to determine the effectiveness of A-LIX technology for removing Cr^{VI}, and MOS technology for removing Cu, Cd, and Cr^{III} from aqueous streams at IWTPs. Reaction rate data were generated for equipment sizing. The equilibrium and kinetic experiments were performed for both extraction and stripping conditions, providing data to prepare the system for fieldwork. Laboratory testing also provided the data needed to choose an extractant for MOS field-testing.

Field-testing occurred at Warner Robins ALC using a slipstream of effluent from the chromium-plating sump to IWTP 2. During this testing, data were collected on the effectiveness of E/A ratio, throughput rates, and impeller tip speeds. A-LIX field-testing was performed first, and then the pilot unit was modified for MOS field-testing on the same slipstream.

C. PILOT PLANT OPERATING EXPERIENCE

1. Description of Unit

The pilot-plant system used for the demonstration operation at Warner Robins is mounted on a portable cart 38 inches by 86 inches and approximately 54 inches high. The primary component of the pilot-plant is a Robatel SX-4.0 four-stage mixer-settler. Support equipment for the process includes tanks, pumps, and filters. Instrumentation includes pH

meters, flowmeters, pressure gages, and temperature indicators. The pilot plant is designed to operate continuously at flow rates up to 1.5 liters per minute.

a. Mixer-Settler. Each of the four stages of the Robatel SX-4.0 mixer-settler is machined from a solid block of polypropylene. Figure 11 provides a simplified depiction of the unit, and Table 5 lists its nominal specifications. A mixer-settler is a liquid-liquid contactor composed of two separate portions as described below:

The Mixer

(1) Role

The mixer produces an emulsion of the two immiscible phases (aqueous and extractant). Its role is to establish intimate contact between the two phases to facilitate mass transfer of one or more solutes.

(2) Composition

The mixer is composed of the following components:

- The mixing chamber, equipped with antivortex baffles
- A feeding system for the two phases in the lower portion of the chamber
- A turbine to assure thorough mixing and to pump the two phases
- A weir over which the emulsion flows towards the corresponding settler

The Settler

(a) Role

The settler separates the two phases previously contacted and emulsified in the mixer.

(b) Composition

The Settler is composed of the following parts:

- A settling chamber which assures sufficient residence time for decantation
- Coalescence plates which accelerate the separation
- Overflow weirs: discharge the two phases separately to adjacent stages or out of the unit.

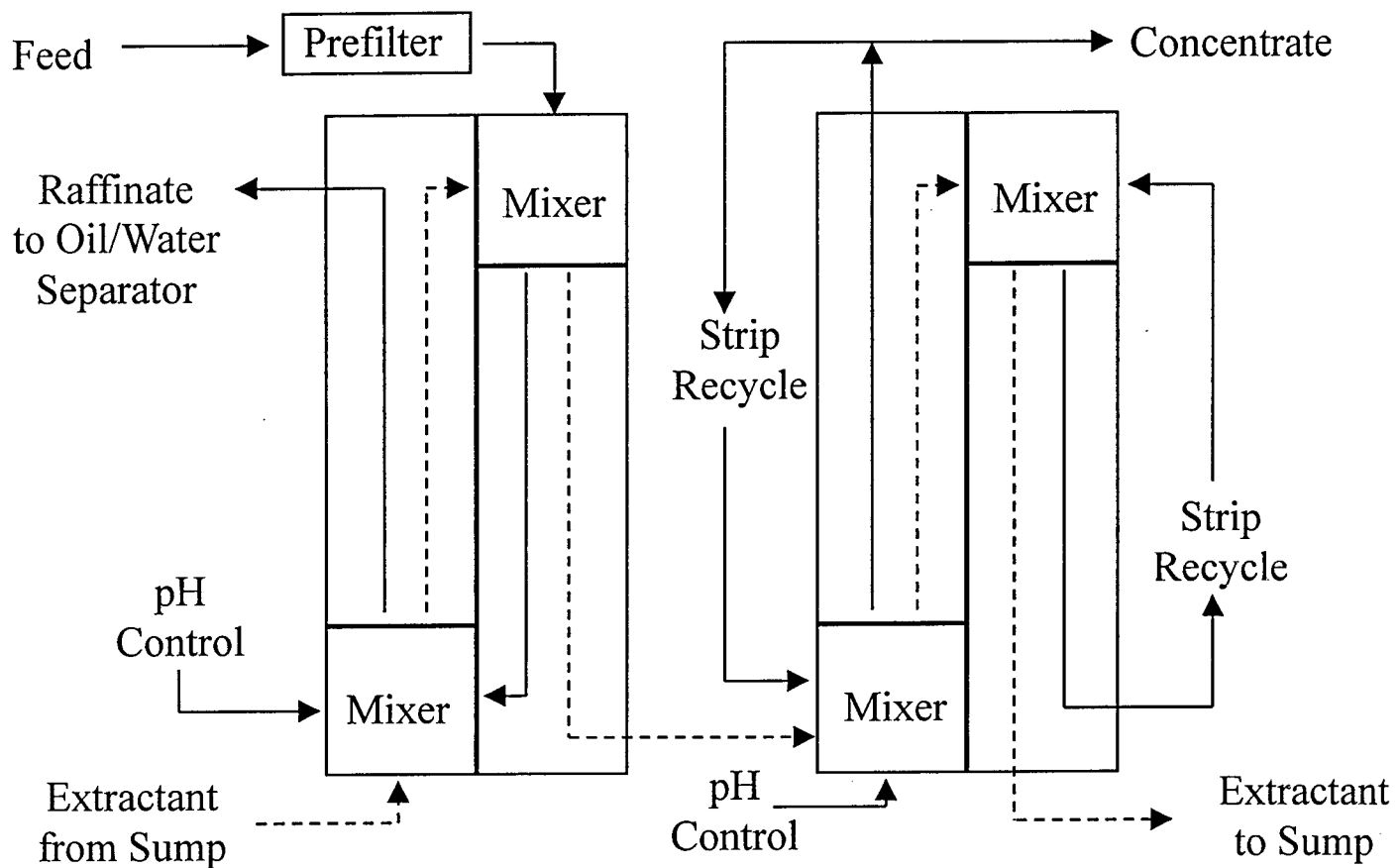


Figure 11. A-LIX Test System.

TABLE 5. NOMINAL SPECIFICATIONS OF THE MIXER-SETTLER.

Volume of each mixing chamber	2.3 liters
Volume of each settling chamber	11.0 liters
Total operating volume of each stage	12.5 liters
Surface area of each settling chamber	1000 cm ²
Total nominal flow rate	40 to 80 liters/hour
Mixing turbine diameter	38 mm
Mixing turbine rotational speed	800 rpm
Nominal turbine rotational speed	1000 to 2000 rpm
Total weight of 4 stages, empty	70 kg
Seals	Teflon encapsulated O-rings
Mixer Motors/speed control	AT 76/35 F; 9W; IP 44 enclosure; 240 volts, delta configuration wiring; 2 ABB AC variable frequency drives, Model #ACS 200, 230 volt, single phase, 60 Hz input
Special features	Recycling of either phase, tapped holes in covers for pH probes

Each Settler has two weirs:

- The light phase weir is composed of a simple overflow weir whose height is fixed.
- The heavy phase weir is composed of a well into which the heavy phase exits several millimeters from the bottom of the Settler. In this well is the actual weir, composed of an adjustable tube supported by a nut. Rotation of this nut adjusts the height of the liquid in the well, and consequently the interphase position in the Settler by hydrostatic equilibrium.

Generally, mixer-settlers are arranged in a head-to-tail orientation that offers many advantages.

- Compact installation
- Simplified industrial construction
- Possibility of circulating the two liquid phases countercurrently.

b. Pumping and Flow Control. Feed and extractant pumping were done using two Cole-Parmer gear pumps (Model 7144-05, head #185-000). These pumps were capable of providing between 0 and 1500 ml/min. All Cole-Parmer pumps were controlled using Cole-Parmer variable speed gear pump controllers (model 7144-08). The acid or base addition for pH control was accomplished using a Mec-o-matic Dolphin 50 peristaltic pump capable of delivering 160 ml/min. This pump was controlled using the pH controller mentioned below. There was no pumping done from the unit to the various holding tanks or between stages. This was all done by gravity.

c. pH Control. The pH was controlled between 3.5 and 6 for the A-LIX extractions using 10 percent sulfuric acid. The pH for the MOS extractions was controlled between 9 and 10 using 10 percent sodium hydroxide solution. Both used a Cole-Parmer pH controller (Model 5652-10) whose output controlled the peristaltic pump mentioned earlier. The pump discharged into the mixer receiving the fresh extractant near the impeller during the A-LIX tests, and into the mixer receiving the fresh feed during the MOS tests.

d. Tanks. The pilot plant used several polypropylene process tanks varying in size from 6 gallons to 11 gallons. They were compatible with the feed stream, the extractant, the stripping solution, the raffinate, and the dilute caustic used for pH control. The sulfuric acid was fed from a heavy 3-liter polyethylene bottle.

e. Filters. There are polypropylene particle filters located on the feed inlet to the process. The filter housings are PVC. These filters remove particulate and debris which are frequently present in the chromium sump.

2. General Description of Operations

During the four months of testing, the pilot unit ran steadily and needed little attention to maintain a particular operating configuration. For instance, once set, the liquids flowed under gravity from stage to stage without plugging. Also, once set, the interfaces between the aqueous and extractant phases remained steady in the settlers. No flooding in any of

the tanks or mixer-settlers occurred. Other than calibration correction (accounted for), the stirrer-pumps performed quite well. During a daylong test, they varied no more than 1 rpm from their set points.

Because the automatic readouts for the impeller speeds seemed unreasonably low, the impellers were recalibrated. To accomplish this, reflective tape was placed on an impeller shaft, and a hand held tachometer was used to measure the rpms. This was done for an extraction unit impeller and for a stripping unit impeller (they are controlled in pairs). Several data points were taken to produce equations so that all automatic rpm readouts could be converted to actual rpms.

To avoid upsets, and provide more uniform test conditions, a few adjustments were made to the system. Because the pilot plant was operated in a truck, undesired liquid motion occurred that would not have occurred if the unit had been situated on a solid floor. To minimize the movement of the truck bed, jack stands were positioned under either side of the bed, and a wood pallet with shims was positioned under the rear step of the truck bed. To eliminate the possibility of aqueous phase interaction between the first stripping unit and the adjacent extraction unit and adjacent stripping unit, the weirs used to control aqueous flows between these units were replaced with plugs. These alterations took place part way through the A-LIX testing. The resulting improvements in system performance are discussed in Section 3.1.1.

There was an unacceptable buildup of extractant in the intermediate raffinate storage tank. This was due to entrained extractant droplets in the raffinate, and forced the operation of the unit at lower feed rates than were intended. To solve this problem an entrainment coalescing oil/water separator was added to the unit. This oil/water separator was designed to provide raffinate with less than 10-ppm of oil. It also allows for the recovery of entrained extractant which is preferable over other cleanup methods, such as activated carbon, that result in the loss of the entrained extractant and the cost of spent carbon filters.

a. Feed Water. The wastewater for the field-testing was a slipstream collected from the effluent of the chromium plating bath rinse water (IWTP 2, Plating Effluent). This water contained approximately 7-ppm chromium as Cr^{VI} . The feed was filtered to remove solids prior to entering the pilot process. A typical composition of this stream is listed below along with the current NPDES limits.

<u>TOXIC METAL</u>	<u>CONCENTRATION (ppm)</u>	<u>NPDES LIMIT (ppm)</u>
Cu ^{II}	0.060	0.050
Cr ^{III}	0.80	0.100
Cr ^{VI}	7.0	0.100
Cd ^{II}	0.003	0.020
Pb ^{II}	< 0.03	0.100

Feed wastewater was treated by the A-LIX or MOS process, sampled and returned to the source downstream of the feed point.

b. Sampling. Samples were collected and analyzed after the system had time to approach steady state conditions. These samples were taken from the settler section farthest from the mixer using rinsed 50 cc syringes. The syringes were wiped using paper towels and the samples were discharged into the sample bottles. Samples of the following were taken:

- Extractant phase
- Extraction raffinate
- Final raffinate (post-oil/water separator)
- Stripping solution
- Feed solution

In addition, mixer emulsions were sampled and E/A ratios recorded.

c. Analytical Procedures. A-LIX testing required analyses of Cr^{VI} in the feed, raffinate and stripping solution. The Hach Diphenylcarbazide Colorimetric method was used for all Cr^{VI} analysis. This technique allowed Cr^{VI} concentrations from 0.01 to 0.60-ppm to be determined. With simple dilutions, more highly concentrated samples were brought into this range. This method was ideal for field-testing.

MOS testing required analyses for total Cr, Cu^{II}, Cd^{II} and Fe. Preliminary values of Cr concentrations were determined on site. This was accomplished by converting Cr^{III} to Cr^{VI} by hypobromite oxidation and analyzing for Cr^{VI} using the Hach method described above. An

ICAP (Inductively Coupled Argon Plasma Elemental Analysis Technique) analyzer located in Columbus was used for metal ion analyses.

3. Test Plans

The A-LIX field-testing matrix is shown in Table 6. The MOS testing matrix is shown in Table 7.

D. RESULTS AND DISCUSSION OF PILOT PLANT DEMONSTRATION

1. A-LIX

a. Results. The operating conditions for each of the A-LIX test runs are shown with their corresponding Cr^{VI} raffinate concentrations in Table 8. The A-LIX system attained the 50-ppb target Cr^{VI} concentration during the majority of the test runs.

The results presented in Table 8 are divided into two sections based upon when the data was collected in relation to process modifications made on June 2. These modifications included stabilization of the truck and elimination of possible interaction (spillage) between the aqueous phases of the first stripping stage and its adjacent extraction stage and stripping stage. In addition to these modifications, a process modification was implemented whereby further testing included acidification of the feed stream with 10 percent sulfuric acid to a pH of approximately 3.5.

A more uniform raffinate was the most significant result of the above modifications. Prior to the changes, the standard deviation of Cr^{VI} concentrations in the raffinate averaged 22-ppb during runs that met the target average raffinate concentration of 50-ppb. It is expected that additional runs would have met the 50-ppb Cr^{VI} target if concentrated strip solution spillover had not led to a few high concentrations raising the average raffinate concentration. After the system modifications, the average standard deviation was 10-ppb for runs that met the 50-ppb Cr^{VI} target raffinate concentration. Due to the range in values of flowrates and feed

TABLE 6. A-LIX FIELD-TESTING MATRIX.

TEST NUMBER	CONDITIONS	OBJECTIVE
Run #1	Center Point; Feed throughput = 500 ml/min, E/A = 1/5, 5% Alamine 336 [®] extractant solution, 2 extraction stages. 2 stripping stages, strip pH > 11, strip recycle rate = 700 ml/min.	Confirm lab findings. Calibrate unit. Evaluate system performance using continuous process stream. Observe physical behavior of system.
Run #2	Feed throughput = 500 ml/min, E/A=1/7, 5% extractant	Evaluate system using the 1/7 E/A ratio.
Run #3, 4	Maximum throughput, E/A = 1/5, 5% extractant	Evaluate system using the 1/5 E/A ratio. Determine maximum throughput.
Runs #5	Feed throughput = 500 ml/min, E/A=1/9, 5% extractant	Determine the effectiveness of the unit using the 1/9 E/A ratio.
Runs #6	Feed throughput = 500 ml/min, E/A=1/5, 5% extractant. Spike strip #1 to ~10,000-ppm Cr ^{VI}	Evaluate system ability to operate with concentrated strip conditions.
Runs #7	Feed throughput = 500 ml/min, E/A=1/5, 5% extractant. Spike strip #1 to ~20,000-ppm Cr ^{VI}	Evaluate system ability to operate with concentrated strip conditions.

TABLE 7. MOS FIELD-TESTING MATRIX.

<i>TEST NUMBER</i>	CONDITIONS	OBJECTIVE
Run #1	Center point; Feed throughput = 1000 ml/min, E/A = 1/10, 5% NTHA-7 extractant solution, 2 extraction stages. 5% sulfuric acid strip solution. Ferrous sulfate added to feed tank.	Confirm lab findings. Calibrate unit. Evaluate system performance using continuous process stream. Observe physical behavior of system.
Run #2	Feed throughput = 500 ml/min, E/A = 1/5, 5% extractant. 5% sulfuric acid strip solution. Ferrous sulfate added in line to feed.	Determine effect of in line addition of Fe^{2+} .
Run #3	Feed throughput = 500 ml/min, E/A = 1/5, 5% extractant. 10% sulfuric acid strip solution. Ferrous sulfate added in line to feed.	Determine system effectiveness with higher acid concentration in strip solution.
Runs #4	Feed throughput = 700 ml/min, E/A = 1/7, 5% extractant. 10% sulfuric acid strip solution. Ferrous sulfate added in line to feed.	Test ability of system to operate at higher throughput.
Runs #5	Feed throughput = 700 ml/min, E/A = 1/7, 5% extractant. Chloride ion added to 10% sulfuric acid strip solution. Ferrous sulfate added in line to feed.	Determine if chloride ion produces better stripping performance.
Run #6	Feed throughput = 700 ml/min, E/A = 1/7, 5% extractant. Chloride ion added to 10% sulfuric acid strip solution. Ferrous sulfate added in line to feed. 2-ppm each of Cu and Cd added to feed.	Test synergy of Cd and Cu on Cr^{III} removal.

TABLE 8. RESULTS OF A-LIX FIELD-TESTING.

Date	Cr(VI) ppm	Feed Flow Ml/min	PH	E/A Ratio	Raffinate Cr(VI), ppb Average
4/30/97	10.0	320	6.5	1/3	23
5/2/97	7.8	280	4.0	1/4	14
5/5/97	5.5	335	5.5	1/4	34
5/5/97	4.5	400	9.0	1/5	40
5/6/97	5.0	540	6.0	1/5	20
5/6/97	3.0	540	7.0	1/5	64
5/7/97	1.8	514	4.5	1/5	14
5/7/97	8.4	490	4.5	1/5	43
5/7/97	8.3	570	4.5	1/7	34
5/8/97	9.0	520	5.8	1/6	100
5/9/97	9.4	389	4.0	1/5	21
5/9/97	6.9	467	4.0	1/5	45
5/12/97	8.5	542	5.5	2/9	93
5/12/97	8.5	542	4.5	1/4	112
5/12/97	8.0	654	4.5	1/4	40
5/13/97	6.4	691	6.0	1/4	31
5/13/97	5.0	691	6.0	1/7	103
5/14/97	9.7	419	5.0	1/8	482
5/15/97	2.7	368	5.0	1/10	172
5/15/97	2.7	368	5.0	1/10	150
Average	6.6	482	5.3	1/5	82
6/3/97	3.9	505	3.5	1/5	37
6/4/97	2.9	516	3.5	1/5	0
6/4/97	6.4	516	3.5	1/5	14
6/4/97	6.4	516	3.5	1/7	25
6/9/97	10.5	775	3.5	1/6	178
6/11/97	7.0	646	3.2	1/6	40
6/11/97	4.6	644	3.3	1/6	27
6/11/97	4.6	505	3.2	1/9	32
6/12/97	6.4	514	3.5	2/9	18
6/13/97	6.4	500	3.3	1/4	12
Average	5.9	564	3.4	1/6	38

concentrations, it is unclear whether acidification of the feed resulted in better system performance.

2. Conditions

a. pH. Based on the chemistry of the A-LIX process (see Section III.B.1), it is clear that a proton is needed for every chromate ion extracted. To ensure that proton availability was not limiting chromate extraction, the feed was acidified beginning on June 2. Prior to this modification, acid was only added to the second extraction unit to maintain a pH in the mixer of 3.5. At the varying feed pHs (Table 8) that had been entering the system, it was possible that a lack of protons limited the ability of the Alamine 336[®] to extract the chromate ions. At a pH of 3.5, excess protons were available so that the chromate ion extraction could not be limited by proton scarcity.

Results did not demonstrate a clear improvement in Cr^{VI} removal when the pH of the feed was controlled at 3.5. More testing would be required to guarantee the completeness of these results, but sulfuric acid use would be greatly reduced if the target extraction pH is 4.5. In addition, sodium hydroxide use would be reduced if less acid were used.

The two stripping units functioned without any problems during the A-LIX field-testing. Manual additions of 10 percent NaOH were used to maintain a pH of at least 11 in each unit. In a similar manner, but less frequently, additions of 10 percent Na₂CO₃ were added when the buffering capacity of the strip solution diminished. To maintain a constant aqueous volume, strip solution was removed in an amount equivalent to the amount of liquid added.

b. Extractant Concentration. During the first few days of operation, the process ran with a 2 percent Alamine 336[®] extractant solution. At this low concentration, it was not possible to operate at E/A ratios of 1/5 or lower. Because of this, the remaining tests were run with a 5 percent Alamine 336[®] extractant solution. Extractant concentration is most meaningful when considered with the E/A ratio because together they provide a measure of the amount of extractant available for a given amount of aqueous flow. Such a measure can be an indication of whether there is a sufficient excess of extractant available for Cr^{VI} removal.

c. E/A Ratio. Figure 12 shows how varying the E/A ratio affected the performance of the A-LIX system. It is important to note that the feed throughput must also be considered when looking at the influence of the A/E ratio on the raffinate concentration. Prior to the process changes mentioned above, the system produced an acceptable effluent when the A/E ratio was less than 6, and the feed throughput was less than 500 ml/min. After the process changes, there was only one run that did not have an average effluent concentration below 50-ppb. This run was most likely caused by insufficient phase mixing at the high feed throughput and an above average feed concentration, 775 ml/min and 10.5-ppb Cr^{VI} respectively. Values as high as 646 ml/min feed throughput, and 9/1 A/E ratio were obtained in runs that produced acceptable effluent concentrations. These parameter values indicate that a 600 ml/min feed throughput and 6/1 A/E ratio are conservative recommendations for a full scale A-LIX system.

d. Throughput Rates. Measurement of throughput rates provided the nominal retention time, τ , in each of the various sections of the system. Each mixer was operated with τ equal to about 3 minutes, and each settler with τ equal to about 15 minutes. Higher throughputs produced lower retention times, but resulted in emulsion carry over to the raffinate. Therefore, improved engineering design enhancements in phase coalescence would be required if higher throughput rates are desired. Data indicate that chemical equilibria are not limiting at these conditions.

e. Impeller Tip Speed. By varying the impeller tip speeds in the mixing chambers of the extraction units, it was found that 1152 rpm produced too fine of an emulsion that led to a hazy raffinate. A small reduction in the impeller tip speed to 1125 rpm produced a clear raffinate. Based on this finding, further tests were performed at this lower rate.

Limiting the mixing rates in the stripping units was not the slow breaking of fine emulsions, but the aspiration of air into the mixing chambers. Because each impeller works as a pump, too high of an impeller speed pumps liquid from an adjoining unit faster than it spills over the dividing weir. As a result, air is pulled into the mixing chamber, leading to surging flows, and inefficient mass transfer. Therefore, pump rates need to be matched to the feed rates to avoid excessive air aspiration.

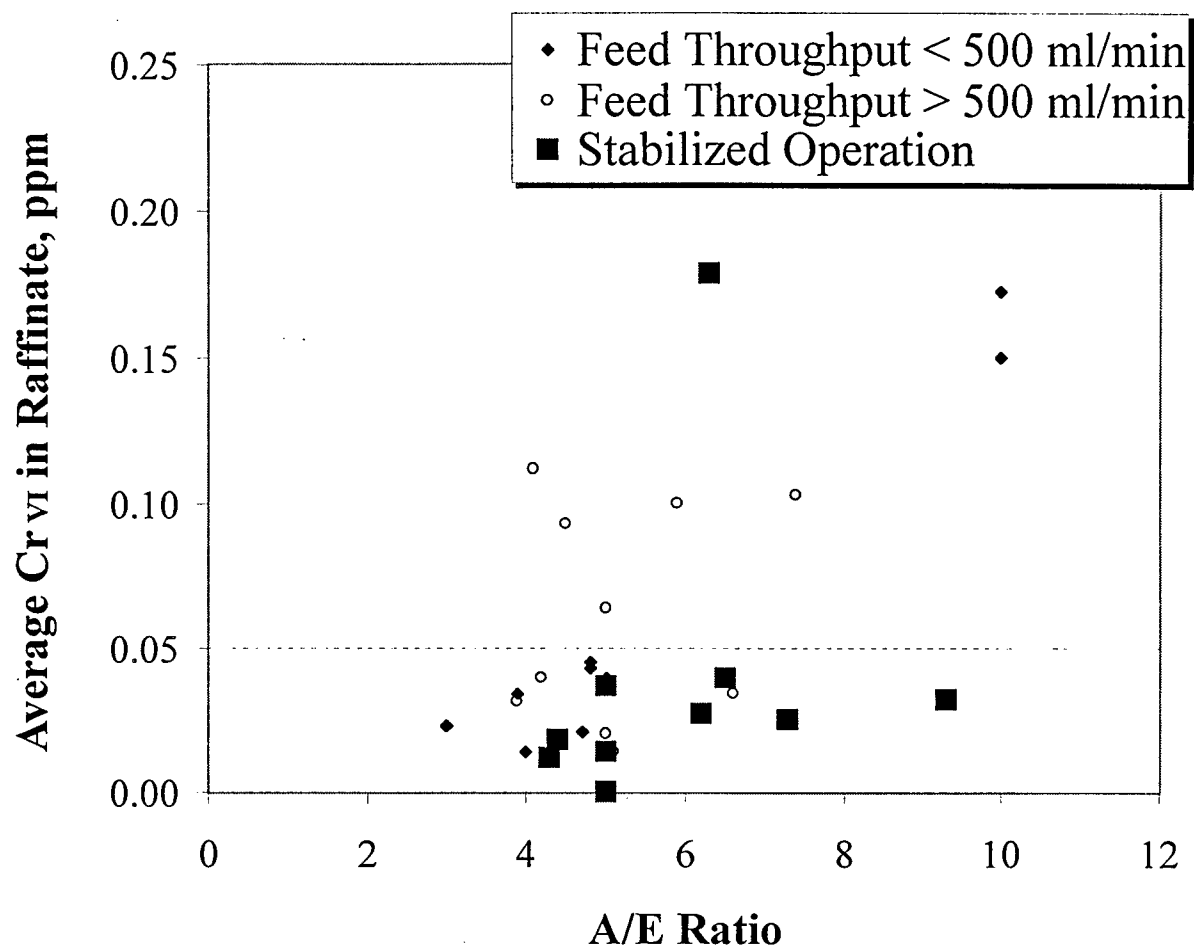


Figure 12. A-LIX Results: Raffinate Concentrations.

f. Product Concentration. Figure 13 shows how the concentration of Cr^{VI} in the first stripping unit continually increased during A-LIX operation. To show that the system could produce a highly concentrated Cr^{VI} solution, and because it would take excessive pilot plant operating time to reach such a concentration, the strip solution in the first stripping unit was spiked with $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$. The strip solution was first spiked to ~10,000-ppm Cr^{VI} and then to ~20,000-ppm Cr^{VI} . As Figure 14 shows, the system produced a consistent raffinate of low Cr^{VI} concentration. This figure also clearly supports the need for two extraction stages. With a feed concentration of about 6.4-ppm Cr^{VI} , the concentration after one stage was about 0.180-ppm and the concentration after the second stage was about 0.015-ppm.

In order to reuse the concentrated Cr^{VI} strip solution, it is necessary to know the concentrations of other species present. Results from analysis of the strip solution just prior to the Cr^{VI} spike are shown in Table 9. Most metals were accumulated in only minor amounts, and had already reached their solubility limits. Total organic carbon and total Kjeldahl nitrogen are also likely at their peak concentrations based on the solubility of these components in the extractant phase. One constituent that should be noted for its accumulation is sulfate, which was concentrated to 15,500-ppm. This is a result of sulfate ions undergoing extraction and stripping in the same manner as chromate ions. Because sulfuric acid was used to control pH in the extraction units, sulfate ions were available in much higher concentrations than chromate ions. Alamine 336® preferentially extracted chromate ions, but there was still enough of the extractant available to transport a significant amount of sulfate ions. The sulfate accumulation rate in the strip solution would be greatly reduced if the pH in the extraction units were maintained at 4.5 rather than 3.5.

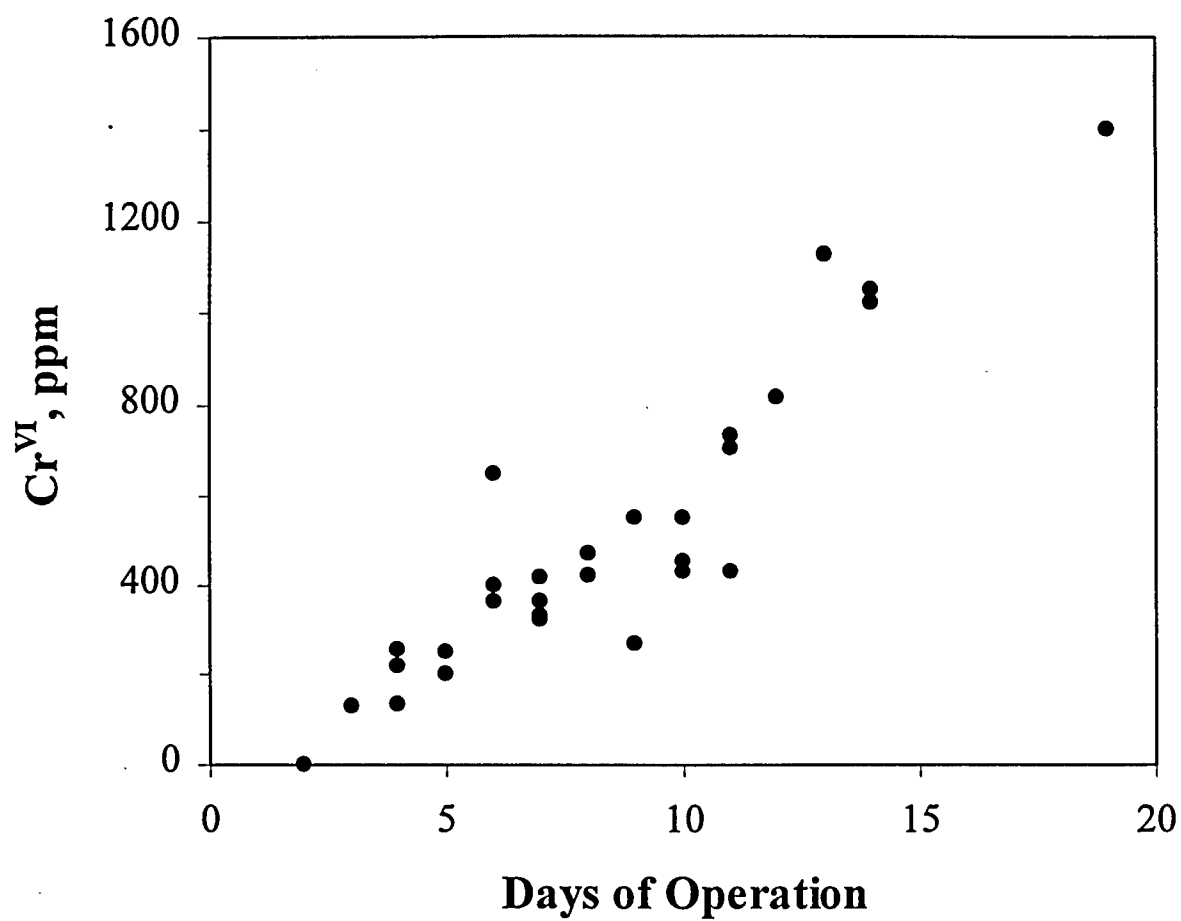


Figure 13. A-LIX Results: Cr^{VI} Accumulation in the First Stripping Stage.

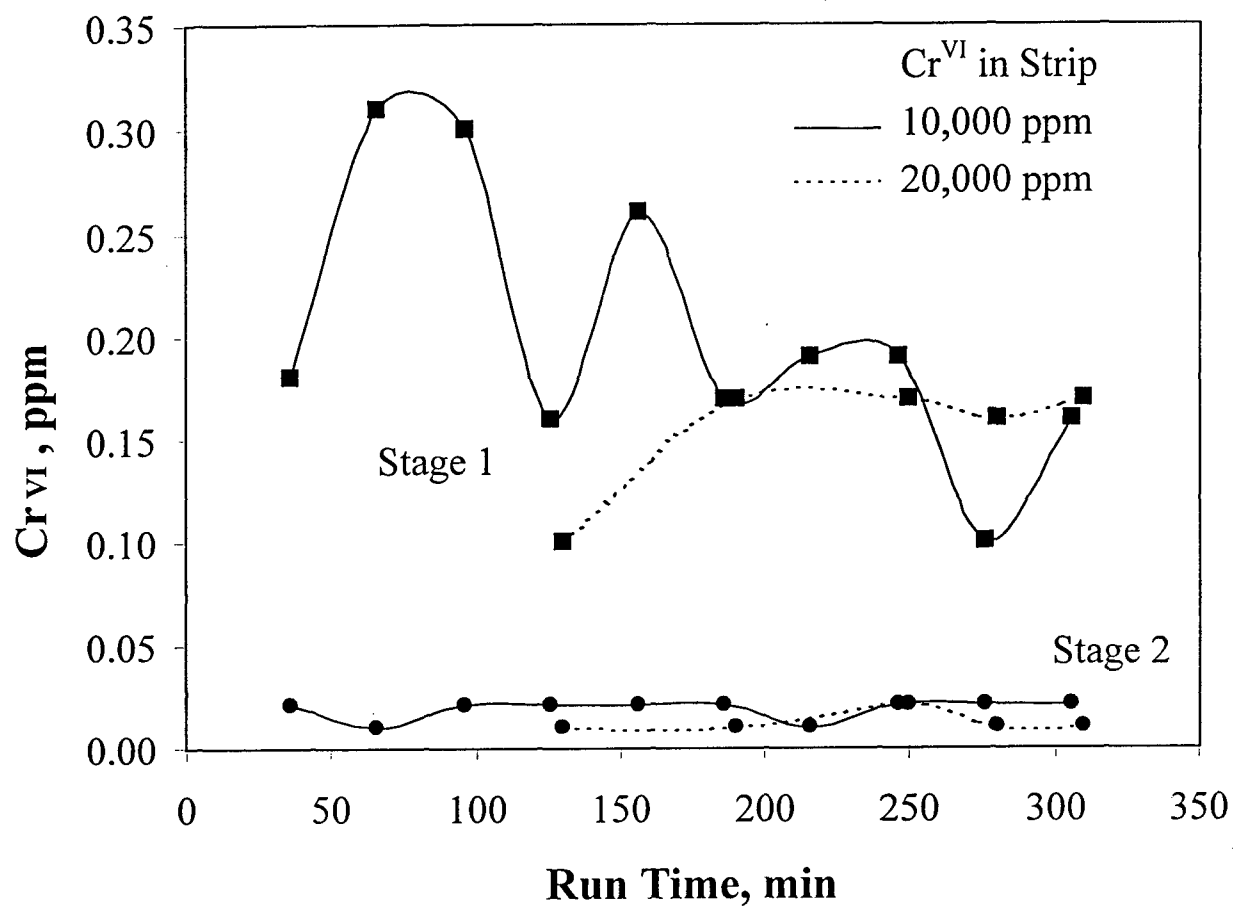


Figure 14. A-LIX Removal of Cr^{VI} from a Feed Concentration of 6.4 ppm.

TABLE 9. ACCUMULATED SPECIES IN THE STRIP SOLUTION.

Constituent	Concentration, ppm
Total Organic Carbon	613
Fluoride	1.95
Sulfate	15,500
Total Kjeldahl Nitrogen	20
Aluminum	8.09
Calcium	11.6
Cadmium	< 0.01
Chromium (VI)	1,400
Copper	0.17
Iron	0.84
Magnesium	1.30
Manganese	0.12
Nickel	0.97
Lead	0.69
Zinc	0.25

g. Technical Conclusions. The results of the A-LIX field-testing indicate that a 50-ppb Cr^{VI} effluent target can be consistently met under the following pilot plant operating conditions:

- Feed throughput of 600 ml/min or less
- E/A ratio of at least 1/6
- Extraction pH of ~4.5, and strip pH of ~11
- 5 percent Alamine 336[®] concentration
- 2 Extraction units

In addition, it was demonstrated that the system could produce a concentrated Cr^{VI} product of at least 20,000-ppm without disrupting the production of the <50-ppb effluent.

3. MOS

a. Results. MOS involves complex kinetics reaction pathways and requires additional engineering before it can consistently extract and concentrate Cr^{III}. The target Cr^{III} raffinate concentration was <50 ppb. This target was not consistently achieved during pilot

testing. NTHA-7 was chosen as the extractant and while data showed a reduction in Cr^{III} in the raffinate, concentrations fluctuated considerably. Difficulties encountered included Cr^{III} concentration in the feed at less than anticipated levels, large variability in the analytical results, and challenges feeding a ferrous sulfate solution to reduce the Cr^{VI} to Cr^{III} .

The results of the MOS field-testing were not as encouraging as the A-LIX results. Consistent production of raffinate with less than the target concentration of 50-ppb Cr^{III} was not achieved. Extraction results varied considerably during the field-testing, indicating the presence of at least one unknown/new parameter not in control. The results are presented here with discussion of the three corresponding feed conditions.

b. Raw Feed. The extraction results from the testing with raw feed were difficult to obtain due to the very low Cr^{III} levels present. Even so, the data indicate that extraction of Cr^{III} was taking place. The best example is based on the data from August 9th. The feed was found to have 5880 ± 300 -ppb of total Cr, and 4600 ± 600 -ppb of Cr^{VI} . The effluent from the second extraction stage was found to have an average ($n=3$) total Cr concentration of 4700 ± 240 -ppb, and the same quantity of Cr^{VI} as the feed. By subtraction, the Cr^{III} concentrations in the feed and effluent are 1300 ± 670 -ppb and 100 ± 640 -ppb respectively. Certainly the Cr^{III} was extracted, but the uncertainty of these values did not allow the MOS process to be properly evaluated (i.e. 50-ppb target).

c. Ferrous Sulfate Added to Feed Tank. During MOS operation that involved adding ferrous sulfate to the feed tank, two mechanical issues arose which complicated the data analysis and interpretation.

The first issue was the depletion of Cr^{III} in the feed tank. The Cr^{III} would settle and concentrate in the bottom of the feed tank, where the outlet was located. This resulted in the Cr^{III} feed being nonuniform with in a concentrated pulse early in each test run. Only on July 18th was this avoided, by periodically stirring the feed tank. Data from this run showed a Cr^{III} reduction from 1700-ppb in the feed to 430-ppb in the raffinate (75 percent Cr^{III} extraction).

A second issue that arose involved the cluster extractant complex layer (a discrete third phase), which tended to accumulate at the aqueous-extractant interface. This complex was likely composed of oligomeric metal hydroxides interacting with water and extractant at the

liquid-liquid interface. With the inclusion of stoichiometric levels of iron in the system the cluster extractant complex layer grew quickly to occupy the entire aqueous-extractant interface. At first, the cluster extractant complex layer was allowed to accumulate to determine if it would reach a critical mass that would force it to begin flowing over the weir with the extractant phase. Because this did not occur, the mechanical movement of the cluster extractant complex layer forward to the next stage was implemented.

d. In Line Ferrous Sulfate Addition. The continuous in line addition of ferrous sulfate was effective in producing higher levels of Cr^{III} in the influent feed stream, and did so reliably throughout each run.

Because of difficulties in controlling the addition of the concentrated iron solution, there was some variability to the feed Cr^{III} concentration during each run. The Cr^{III} concentration data from the runs under these conditions, along with the data from July 18th are provided in Figure 5. The variation in iron addition produced the varying Cr^{III} concentrations. Constant addition of ferrous sulfate would produce constant Cr^{III} concentrations, an operation expected to be easier to perform at the commercial scale. The operating parameters for the runs depicted in Figure 15 are given in Table 10.

4. Conditions

a. Addition of Ferrous Sulfate. During most of the MOS testing the concentrations of Cr^{VI} and Cr^{III} being discharged by the plating shop were lower than recent averages during the A-LIX testing. Typical concentrations during the MOS testing were 2.2-ppm Cr^{VI} and 0.3-ppm Cr^{III} .

For the first 6 days of testing, the plating shop effluent was used without modification as the feed stream for the pilot unit. With the majority of the chromium in the form of Cr^{VI} , it became clear that the dilutions needed for analysis resulted in the magnitude of Cr^{III} concentrations being similar to the magnitude of experimental error and the detection limit.

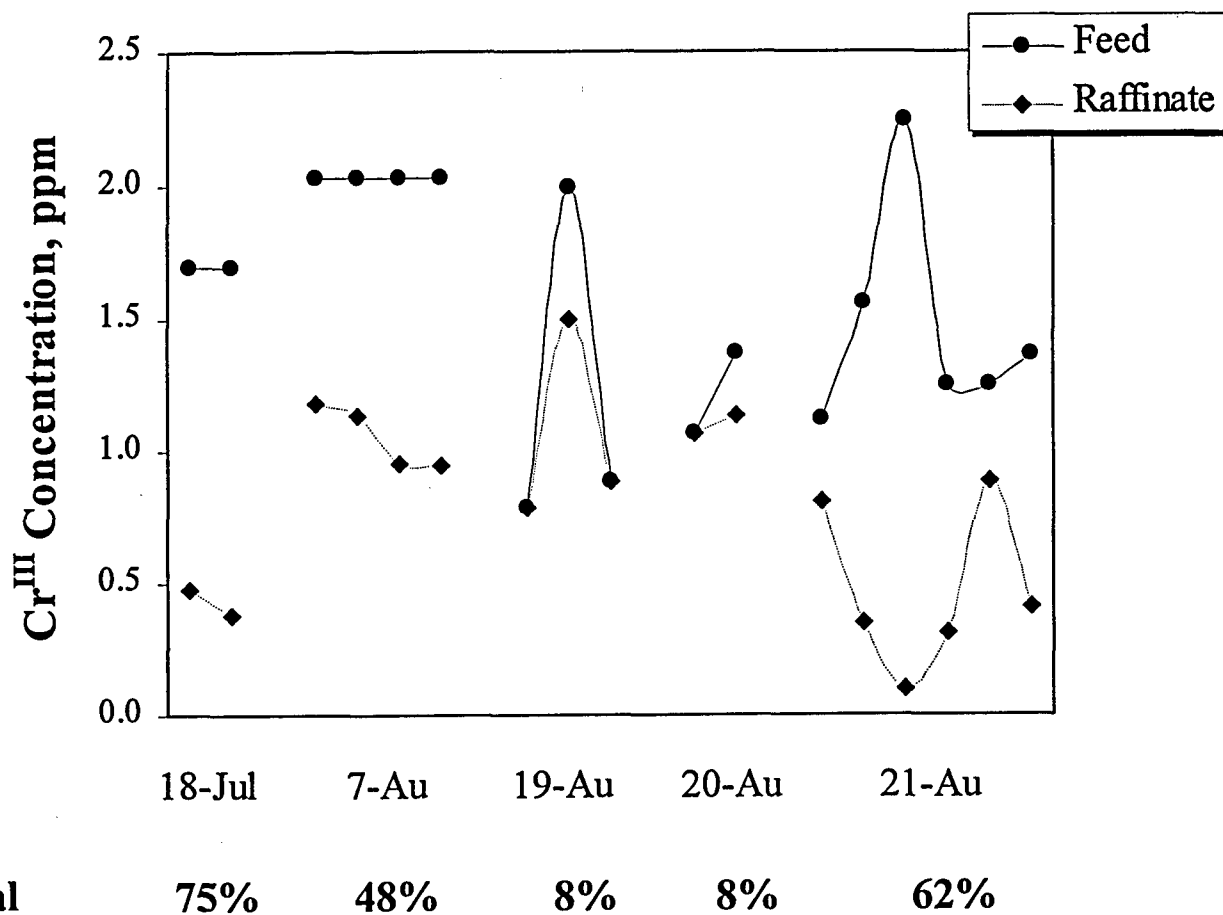


Figure 15. Removal of Cr^{III} using MOS.

TABLE 10. MOS OPERATING PARAMETERS.

Date	Feed		Extractant		Runtime hr:min
	Flow ml/min	pH	Volume in each Ext. Stage, l	E/A ratio	
07/18/97	944	6	1.9	1/10	3:54
08/07/97	491	6	1.7	1/5	5:16
08/19/97	467	5	1.0	1/5	3:57
08/20/97	705	5	1.0	1/7	2:55
08/21/97	672	5	1.0	1/8	2:31
08/21/97	676	5	1.0	1/8	2:36

Because these low values were not representative of average operating conditions, and because the small fraction of chromium found as Cr^{III} caused analytical precision problems, the concentration of Cr^{III} fed to the pilot unit was increased by adding ferrous sulfate to reduce a portion of the Cr^{VI} present in the feed. During the testing, two methods were used for the addition of the ferrous sulfate. From the 7th through the 11th days of operation, ferrous sulfate heptahydrate was added to the feed in the feed tank. For the remainder of the testing a Fe^{II} solution was added directly to the feed stream.

On day 7, the stoichiometric amount of Fe^{II} needed to reduce all of the Cr^{VI} present in the feed was added. On days 8 through 11, twice the stoichiometric amount of Fe^{II} needed to reduce all of the Cr^{VI} present in the feed was added. Also, to help prevent metal hydroxide formation in the feed tank, the pH was adjusted to ~5.5 with 10 percent sulfuric acid.

For in-tank ferrous sulfate addition, it became apparent that the Cr^{VI} reduction reaction took place so quickly that the Cr^{VI} was converted to Cr^{III} within a few minutes, and that the Fe^{III} and Cr^{III} were precipitating to the bottom of the feed tank. For example, on day 8 the Cr^{III} concentration was 1570-ppb in the feed tank soon after the addition of ferrous sulfate, but two hours later the concentration had dropped to 8-ppb. A new method of Fe^{II} addition was needed.

For the remainder of the field-testing, a concentrated (~2100-ppm Fe^{II}) solution of ferrous sulfate was continuously added in line to the feed stream. The junction was inserted into

the feed line at a location that allowed approximately 10 seconds of mixing prior to the feed inlet. This new feed was sampled at the inlet for analysis. The analysis procedure is not instantaneous, but in less than a minute more than 90 percent of the Cr^{VI} had been reduced to Cr^{III} . Residence times in the first mixer were greater than 2.5 minutes. The targeted rate of ferrous sulfate addition was set to provide 5-ppm more Fe^{II} than stoichiometrically needed to reduce all of the Cr^{VI} in the feed. The only exception to this occurred during the final test run when 2-ppm each of Cu and Cd were added to the feed tank. For this run, the targeted rate of Fe^{II} addition was set to 120 percent of the stoichiometric quantity needed for Cr^{VI} reduction.

b. Movement of Cluster Extractant Complex Layer. Although Figure 16 does not clearly demonstrate that Cr^{III} is being stripped from the extractant in the stripping stages, Figures 17 and 18 show how all four metals (Cr^{III} , Cd, Cu, Fe) are accumulating in these stages. As expected, the concentrations of metals accumulated in the first stripping stage are higher. Figure 18 illustrates the results of mechanically moving the cluster extractant complex layer into the first stripping unit. Prior to day 12 of operation, the cluster extractant complex layer was not mechanically aided in its movement to the stripping portion of the pilot plant. On day 12, mechanical assistance allowed the cluster extractant complex layer to travel over the weir, and into the first stripping unit. In the 5 percent sulfuric acid conditions of the stripping unit, the cluster extractant complex immediately dissolved. During all further operations, the cluster extractant complex layer was mechanically assisted into the stripping phase at least every 10 minutes.

The sudden jump in Cr^{III} and Fe concentrations on day 12 indicates that the accumulated cluster extractant complex layer did contain both of these metals, and that a large amount of each became associated with the strip aqueous phase upon cluster extractant complex dissolution. In contrast, the concentrations of Cd and Cu in the strip solution did not show similar increases. However, the concentrations of Cd, Cu and Fe did increase from day 13 to day 14, August 7th to 19th. During this same period, the Cr^{III} concentration declined.

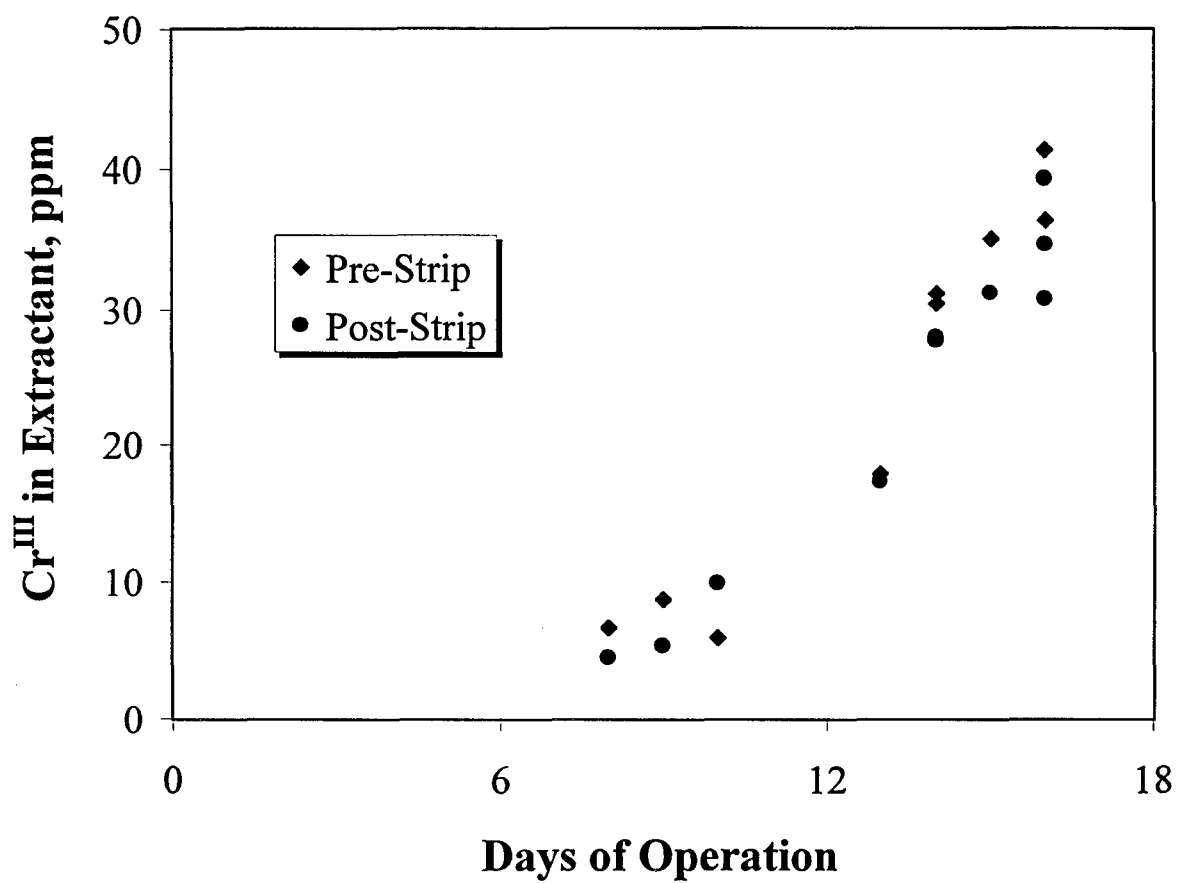


Figure 16. Extractant Accumulation of Cr^{III} during MOS Testing.

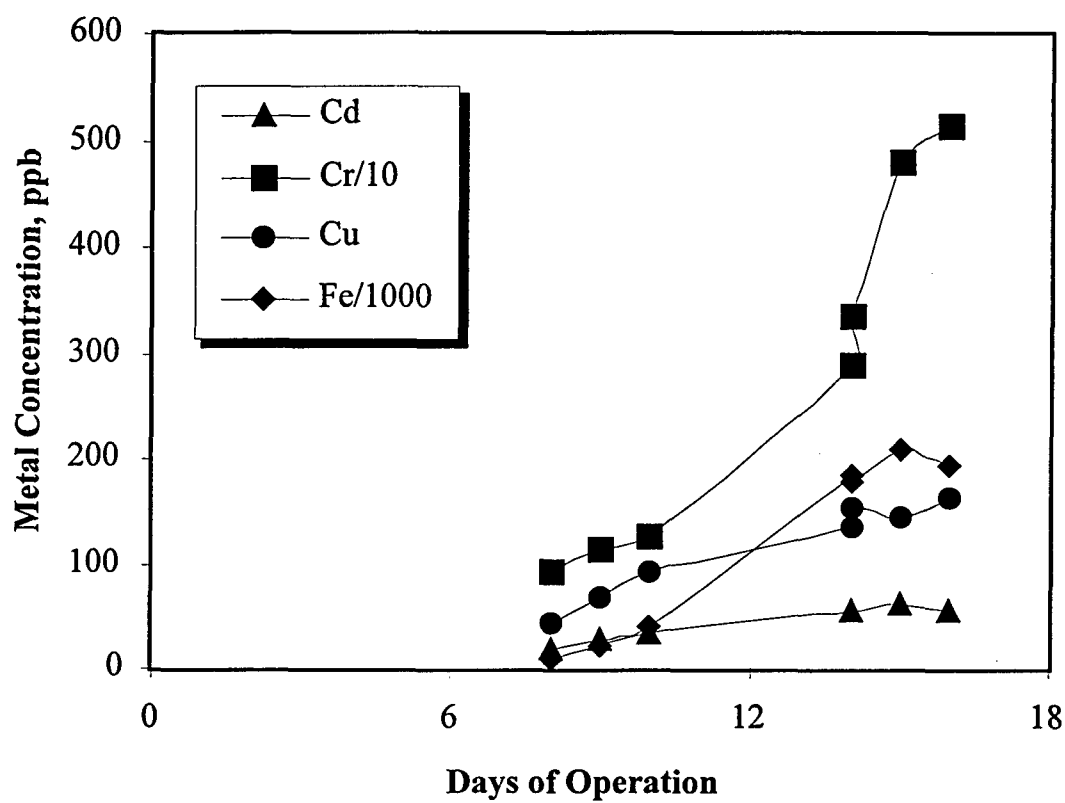


Figure 17. Metals Accumulated in the Second Stripping Stage.

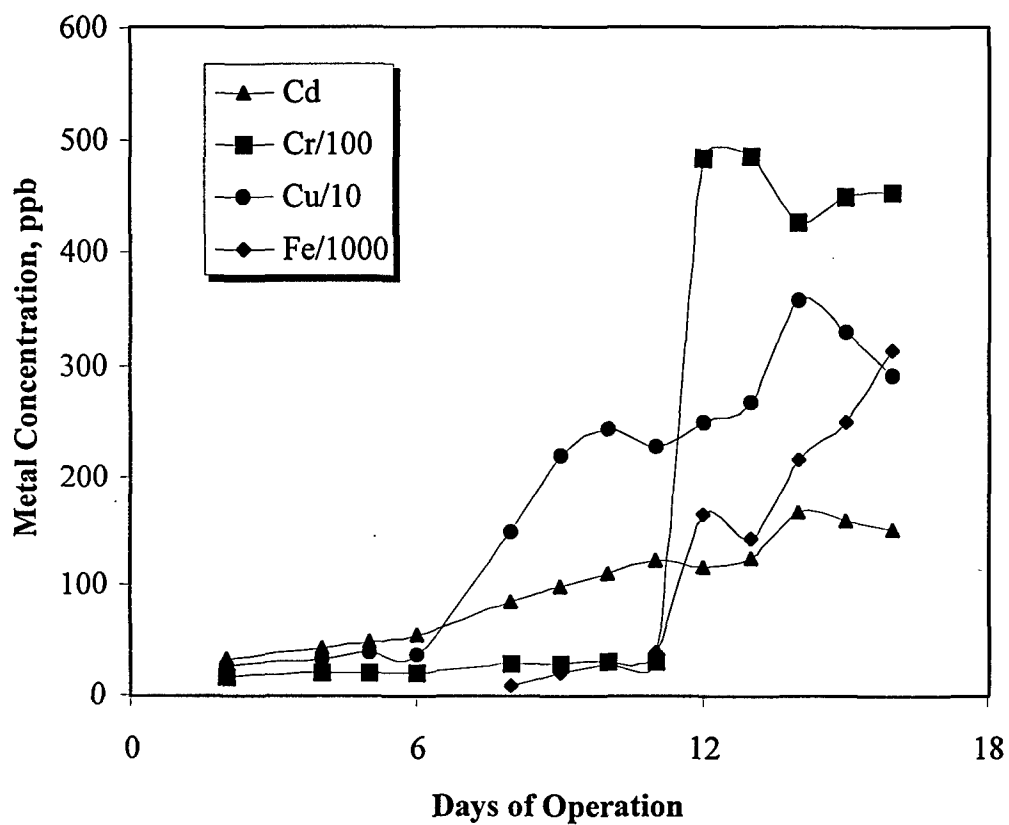


Figure 18. Metals Accumulation in the First Stripping Stage. Beginning on Day 12, the Cluster Extractant Complex Layer was Mechanically Assisted.

Based on Cu concentrations listed in Table 11, it is clear that Cu was in the accumulated cluster extractant complex layer that moved on to the stripping unit on day 12. Because the Cu did not show up in the strip solution (Figure 18) on day 13, it must have remained associated with the extractant after the cluster extractant complex dissolved. This conclusion is fairly well supported by the rise in post-strip extractant phase Cu after day 12.

Concentrations of Cd in the pilot unit were generally quite low, and often below detection limits. Because of this, it is not clear how the Cd behaved with respect to the accumulated cluster extractant complex layer.

c. Strip Solution. A 5 percent sulfuric acid strip solution was used for the majority of the MOS testing. However, insufficient stripping occurred with this strip solution, so two variations were made. For the last three days of testing, the sulfuric acid concentration was increased to 10 percent, and on the final day of testing, sodium chloride was added to the 10 percent sulfuric acid to provide a 3 percent acidic chloride ion concentration.

The addition of chloride ions, to the stripping stages did not seem to improve the stripping ability of the MOS system over 10 percent sulfuric acid. Just prior to testing on August 21st (16th day of operation), sodium chloride was added to bring the chloride ion concentration to about 3 percent. There was not a corresponding decrease in the metal concentrations of the post-strip extractant phase that would indicate improved stripping for these conditions (Table 11).

Doubling the sulfuric acid strip concentration greatly improved Fe^{III} stripping, but had no noticeable effect on Cr^{III} stripping. As shown in Figure 19, the concentrations of iron in the extractant both before and after the stripping stages were between 20 and 70-ppm. With the increased acid concentration, the Fe^{III} concentration in the pre-strip extractant was similar to earlier data, but the post-strip extractant showed no Fe^{III} when analyzed (detection limit 0.9-ppm). Figure 16 depicts the Cr^{III} concentration in the extractant phase both before and after stripping. This plot shows the steady increase in Cr^{III} accumulated in the extractant. While the post-strip concentrations tend to be slightly lower than the pre-strip concentrations, both data sets show the same upward trend. When compared to the iron behavior (Figure 19), it is clear that the doubling of the acid strip concentration had no visible effect on the stripping of Cr^{III} .

TABLE 11. METALS ACCUMULATION IN THE EXTRACTANT PHASE.

	Sample	Day	Cd, ppb	Cr, ppm	Cu, ppb	Fe, ppm
Pre-Strip	7/15/97 18:17	8	11.4	7	388	28
	7/16/97 18:20	9	< 134 (62.2)	9	< 536 (460)	49
	7/17/97 17:13	10	< 134 (57.6)	6	< 536 (331)	29
	8/7/97 18:22	13	< 134 (0)	18	1720	65
	8/19/97 19:45	14	136	30	< 536 (0)	31
	8/19/97 20:10	14	< 134 (4.13)	31	< 536 (0)	32
	8/20/97 20:00	15	< 134 (18.9)	35	< 536 (0)	23
	8/21/97 12:23	16	< 134 (103)	36	< 536 (0)	44
	8/21/97 17:40	16	4700	41	8860	40
Pre-Strip With Clusters	7/15/97 18:40	8	< 134 (85.4)	16	5720	142
	8/7/97 18:23	13	< 134 (0)	27	3140	157
	8/19/97 19:45	14	140	154	< 536 (447)	415
	8/19/97 20:10	14	160	195	5780	439
	8/20/97 20:00	15	183	184	4770	378
	8/21/97 12:30	16	< 134 (99)	98	< 536 (287)	320
	8/21/97 17:40	16	10800	267	16700	744
Post-Strip	7/15/97 18:10	8	< 134 (59.1)	4	< 536 (382)	22
	7/16/97 18:10	9	< 134 (4.46)	5	< 536 (343)	30
	7/17/97 17:13	10	< 134 (0)	10	< 536 (436)	40
	8/7/97 18:35	13	< 134 (0)	17	1690	52
	8/19/97 19:53	14	< 134 (17.8)	28	2200	< 0.9 (0)
	8/19/97 20:12	14	< 134 (133)	28	< 536 (235)	< 0.9 (0)
	8/20/97 20:00	15	135	31	1480	< 0.9 (0)
	8/21/97 12:23	16	193	35	3020	< 0.9 (0)
	8/21/97 16:39	16	< 134 (11.2)	31	< 536 (51.8)	< 0.9 (0)
	8/21/97 17:40	16	< 134 (54.7)	39	< 536 (422)	< 0.9 (0)

Values in () are below method detection limits as indicated.

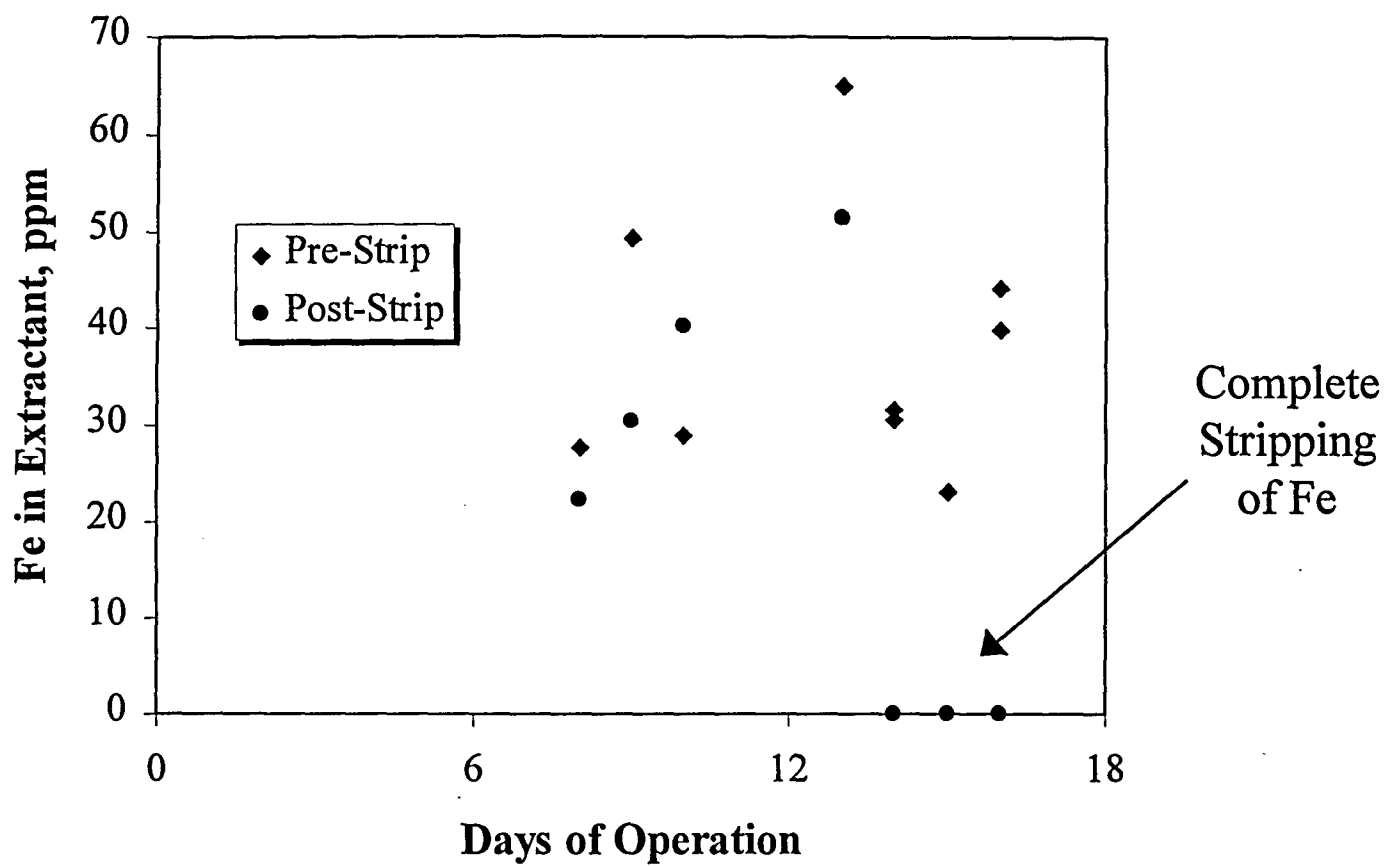


Figure 19. Extractant Accumulation of Iron during MOS Testing.

In Figure 20, the post-strip Cr^{III} concentration in the extractant phase is plotted against the Cr^{III} concentration in the strip solution. These are the extractant and aqueous phases in the second stripping settler. Figure 20 clearly shows that only small amounts of stripping were occurring. In a more ideal situation, the ratio of solute concentrations would heavily favor the stripping solution. For the data shown, the Cr^{III} favors the extractant phase by a ratio of more than 6/1. Since no extraction of Cr^{III} from 10 percent sulfuric acid occurs, this result is understood to mean that the Cr^{III} strip rate is very slow (consistent with the known ligand exchange rate for Cr^{III} compounds). Therefore, it is seen as critical that formation of such complexes be discouraged in favor of Cr^{III} clusters involving faster reacting metal ions such as Fe^{III} . However, the results given above do not fully describe the critical parameters that control such desirable cluster formation.

E. A-LIX ECONOMIC ANALYSIS

A preliminary economic analysis of a full scale A-LIX system was evaluated for installation at the WR-ALC IWTP #2. The following values are the basis for the analysis:

- Feed of 80,000 gpd and 6-ppm Cr^{VI}
- Extraction E/A ratio of 1/6
- Extraction pH of 4.5 and stripping pH of 11
- Mixer residence times of 3 minutes
- Settler residence times of 16 minutes
- 56-ppm extractant phase in raffinate

Figure 21 provides schematics of IWTP 2 before and after A-LIX installation. An illustration of the A-LIX process with process streams is depicted in Figure 22.

Phase 1 of this project reported that current operation of IWTP 2 produces 276 tons per year of wet sludge that can be attributed to Cr^{VI} . This production rate of wet sludge could be eliminated, and replaced by the production of a concentrated sodium chromate solution. This concentrate could be used as a raw material.

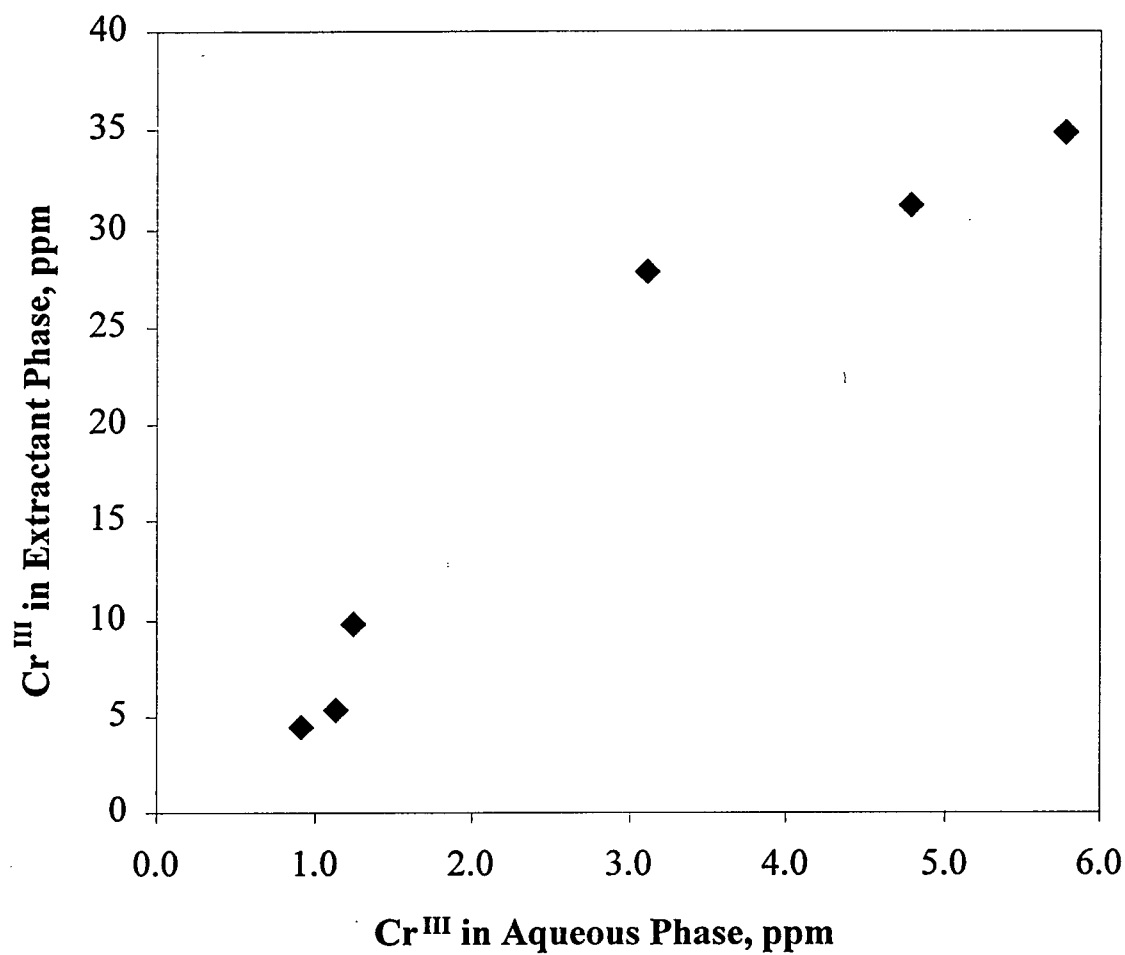


Figure 20. Comparison of the Cr^{III} Accumulation in the Aqueous and Extractant Phases of the Second Stripping Stage.

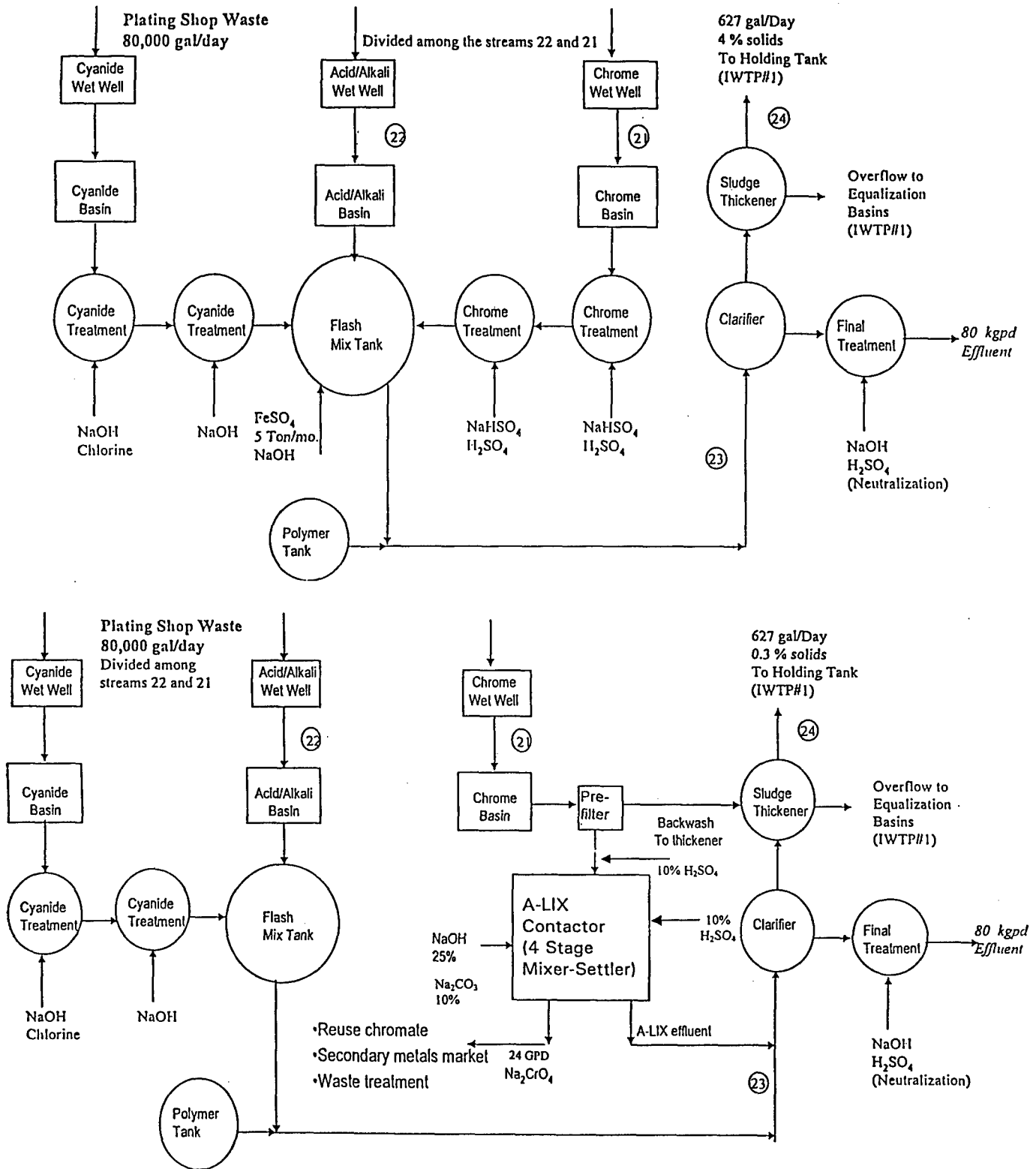


Figure 21. Schematic of IWTP 2 Before (Top) and After (Bottom) A-LIX Installation.

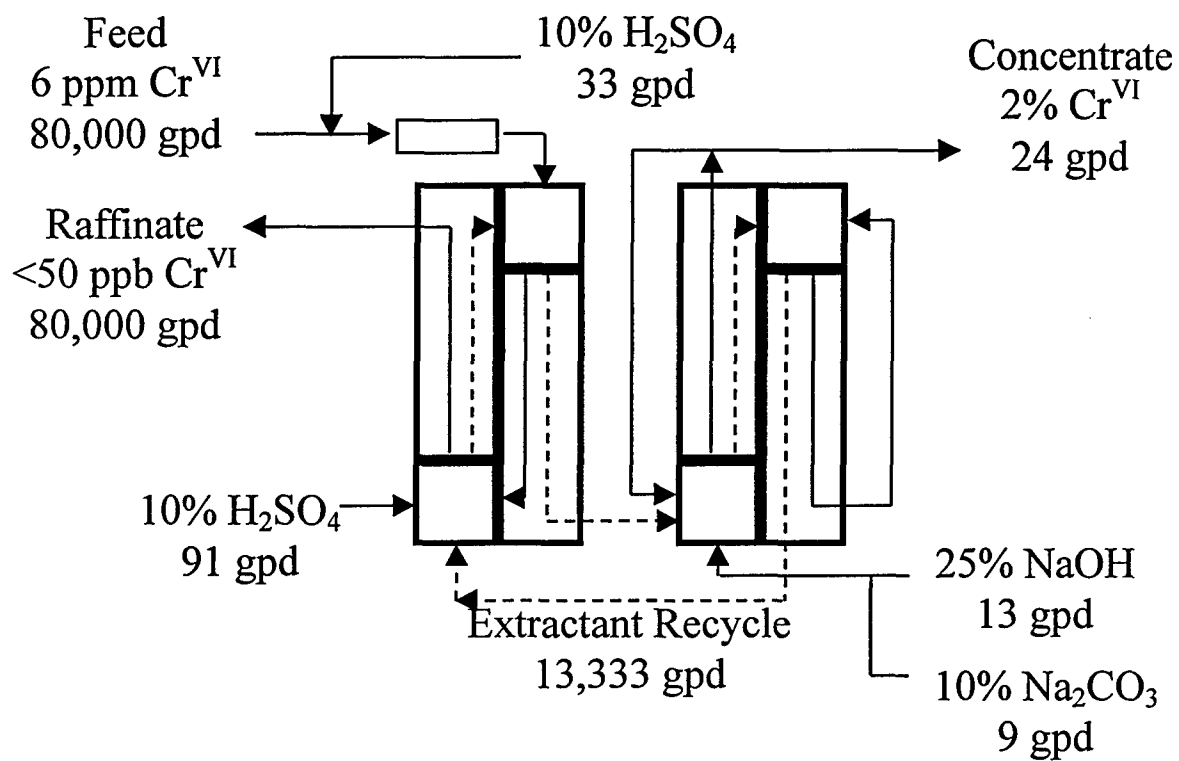


Figure 22. Full Scale A-LIX Process. The Volume of Each Mixer-Settler is about 1100 gal.

The cost of each of the four mixer settlers would be about \$10,000. Including various pumps, tanks, taxes and delivery charges results in an estimated purchased equipment cost of \$96,000. Table 12 summarizes estimated capital costs along with best case and worst case estimates.

Varying the operating parameters has little impact on the total capital investment, TCI, because of the system's relatively small size. This holds true even for parameter ranges where the A-LIX system has not been shown to consistently produce a raffinate with less than 50-ppb Cr^{VI} . For instance, a decrease in the E/A ratio to 1/9 results in only a \$5,000 (1.3 percent) reduction of the TCI. Similarly, a reduction in the residence times to 2 minutes, and 9 minutes would only reduce the TCI by \$25,000 (6.5 percent).

The operating costs for this full-scale A-LIX system are summarized in Table 13. As with the capital costs, the nominal case is listed along with optimistic and conservative cases. The sensitivity of the total annual operating costs, TAOC, to parameter variations are also low. The decrease in the E/A ratio to 1/9 would result in a \$3,900 (6.0 percent) reduction of the TAOC. For the reduced residence times of 2 and 9 minutes, the TAOC decreases by \$2,600 (4.0 percent).

Annual savings of \$121,000 can be realized if WR-ALC does not have to dispose of 276 tons of sludge each year. These savings together with the TCI and TAOC result in estimated payback periods of 4, 7, and 10 years for the best, nominal, and conservative cases respectively. Increases in waste sludge disposal costs would result in the A-LIX system becoming more attractive economically. For example, a 50 percent increase in the disposal costs would reduce the estimated payback periods to 2, 3, and 4 years. Capital cost savings may be possible by complete shop fabrication of the system to minimize field construction and piping costs. This approach could reduce both TCI and the payback period.

Existing facilities treating Cr^{VI} waste, such as WR-ALC, have capital invested in traditional precipitation systems. If a new facility were being evaluated based on the economics of installing an A-LIX system versus installing a precipitation system, the A-LIX system economics would be much more favorable. This would also be true in the case of an existing facility requiring significant investment to continue operating.

TABLE 12. PRELIMINARY ESTIMATE OF CAPITAL COSTS FOR 80,000 gpd A-LIX SYSTEM.

COST ITEM	PE COST REDUCED 25%	NOMINAL CASE	PE COST INCREASED 25%	BASIS
Purchased Equipment (PE)	72,000	96,000	121,000	100.00% of PE Cost
PE Installation	34,000	45,000	57,000	47.00% of PE Cost
Instrumentation and Control	13,000	17,000	22,000	18.00% of PE Cost
Piping	48,000	64,000	80,000	66.00% of PE Cost
Electrical	8,000	11,000	13,000	11.00% of PE Cost
TOTAL DIRECT PLANT COST	175,000	233,000	292,000	
Engineering and Supervision	24,000	32,000	40,000	33.00% of PE Cost
Construction Expense	30,000	40,000	49,000	41.00% of PE Cost
TOTAL DIRECT & INDIRECT COSTS	228,000	305,000	381,000	
Contractors Fees	11,000	15,000	19,000	5.00% of Direct & Indirect Costs
Contingency	23,000	30,000	38,000	10.00% of Direct & Indirect Costs
FIXED CAPITAL INVESTMENT	263,000	350,000	438,000	
Startup Cost	25,000	28,000	30,000	10.00% of PE Cost + 90 Man Days Labor
	4,000	5,000	5,000	Initial Charge of Chemicals
				+ 1 Month Chemical Supply
TOTAL CAPITAL INVESTMENT	\$292,000	\$383,000	\$473,000	

TABLE 13. PRELIMINARY ESTIMATE OF OPERATING COSTS FOR 80,000 gpd A-LIX SYSTEM.

COST ITEM				Basis Quantity	Price per lb		
	Best	Nominal	Conservative		Best	Nominal	Conservative
RAW MATERIALS							
Alamine 336	2,400	2,500	2,700	1023 lb	\$2.35	\$2.48	\$2.61
Decyl alcohol	800	800	900	1023 lb	\$0.76	\$0.80	\$0.84
Aromatic 150	7,400	7,800	8,200	18421 lb	\$0.40	\$0.42	\$0.45
Sulfuric acid, 100 %	1,500	7,800	8,200	40832 lb	\$0.04	\$0.19	\$0.20
Soda ash (Na ₂ CO ₃), 99 %	200	700	700	3132 lb	\$0.08	\$0.21	\$0.22
Sodium hydroxide (NaOH), 76 %	5,200	10,000	10,500	16726 lb	\$0.31	\$0.60	\$0.63
MATERIAL COST SUBTOTAL	17,500	29,600	31,100				
SUBTOTAL, \$ PER 1000 GAL	\$0.60	\$1.01	\$1.07				
UTILITIES Electricity	3,800	4,600	4,600	\$0.06 PER KWHR			
LABOR Operating	6,800	9,100	11,400	\$25.00 PER HR			
	1,000	1,400	1,700	15.00% OF OPERATING LABOR			
MAINTENANCE	10,500	14,000	17,500	4.00% OF FCI			
OPERATING SUPPLIES	1,600	2,100	2,600	15.00% OF MAINTENANCE			
LABORATORY CHARGES	1,000	1,400	1,700	15.00% OF OPERATING LABOR			
WASTEWATER DISPOSAL	(1,000)	0	1,000	\$/year			
INSURANCE	2,600	3,500	4,400	1% OF FCI			
TOTAL ANNUAL OPERATING COSTS	\$44,000	\$65,600	\$76,100				
OPERATING COST, \$ PER 1,000 GAL	\$1.51	\$2.25	\$2.61				

F. CONCLUSIONS AND RECOMMENDATIONS

1. A-LIX

The A-LIX field-testing demonstrated high system operability and excellent Cr^{VI} removal and product concentration. For feed streams with average Cr^{VI} concentrations of 6-ppm, the field unit consistently produced a raffinate having less than 50-ppb Cr^{VI} . At the same time, the system was able to produce a Cr^{VI} concentrate of greater than 20,000-ppm.

Implementation of the A-LIX system has the potential to reduce sludge waste production by 276 tons per year. Rather than producing sludge as the current precipitation process does, the A-LIX system would produce a potentially reusable Cr^{VI} concentrate. The A-LIX process is an excellent technical and good economic solution for reducing USAF chromium plating shop waste.

With the success of the A-LIX pilot plant operation, it is recommended that either OC-ALC, OO-ALC, or WR-ALC be chosen as the site for construction of a prototype A-LIX unit. (At Tinker or Hill, the A-LIX system would take the place of the current Cr^{VI} pretreatment systems.) The unit would be of commercial grade construction and design, and would require minimal operator attention. This prototype unit would be used to generate long-term continuous performance data, and generate Cr^{VI} concentrate for reuse/recycle evaluation. From this system, detailed design and economic analyses could be developed, so that "turn key" units and operational procedures would be available to other sites.

2. MOS

Additional laboratory experiments and field-testing are needed to demonstrate the MOS concept. Laboratory experiments are needed to provide more detailed information on the complex reaction pathways and kinetics to identify process control parameters. Then additional field-testing would be needed to develop and validate the engineering required for this broad spectrum metal recovery system. This technology should find widespread application across DoD and industry.

SECTION IV

ALTERNATIVE CHEMISTRY OF IMPURITY-BASED SCC BLANKET FOR REMOVING TOXIC METALS

A. INTRODUCTION

The field tests were designed to evaluate alternative chemistry in an impurity-based solids contact clarifier (SCC) sludge blanket for removing toxic metals and substantially reducing amounts of metal hydroxide waste. Previously at OC-ALC large amounts of iron and caustic were used to provide a blanket of ferric hydroxide flocs. Currently, OC-ALC is using ferrous sulfate and sodium hydrosulfide to reduce chromium and precipitate metals at a pH of 7.5. Past studies by EG&G have shown this chemistry to reduce sludge formation. OC-ALC switched processes because they were having problems with controlling the process and were generating large quantities of sludge.

1. Objective

The field test objectives were to evaluate process operabilities using reduced ferrous sulfate addition, borax pH control, or two polishing technologies that constitute the impurity-generated SCC blanket technology for the removal of toxic metals. The test also provided technical and economic data for implementing the proposed chemistry using the existing SCCs at OC-ALC and WR-ALC.

The baseline test was compared to ongoing operations at OC-ALC IWTP drawing from the same basin. The baseline test was conducted to build up the solids in the SCC and to form a basis for further testing. The alternative chemistries were compared to the baseline.

2. Background

Field-testing was conducted at the OC-ALC IWTP using a 6 ft. diameter skid-mounted SCC pilot plant constructed similar in design and function to the full-scale SCC installed at the plant. The critical scaling parameter used to design/specify the pilot plant was the settling/sedimentation velocity for the full-scale SCC. The pilot plant feed water used a slipstream from the south equalization basin. Characterization data on this stream are given in

Section IV.C of the Phase I report for this project. In the pilot test, both the ferric-hydroxide-based blanket and impurity-generated blanket processes were used. Reduction of the quantity of ferrous sulfate used was the major sludge blanket modification tested. The ferric hydroxide sludge blanket also serves to remove some metal ions that remain in solution after chemical treatment. Chemical treatment with polishing agents and pH buffering were also tested to evaluate their benefit to reducing the metal effluent concentrations.

The chemical parameters that maximize operability, toxic metal removal levels, and the need for polishing agents were determined. These parameters include pH control using borax buffer and the addition of low levels of polishing agents. The polishing agents tested were phosphate and ISX (Insoluble Starch Xanthate). Flocculent dosage was altered as necessary to minimize entrainment of suspended solids in the SCC effluent. The flocculants used were Betz 1195 and Drew 270, which are currently in use at the OC-ALC IWTP.

3. Approach

The OC-ALC IWTP metal treatment process fulfills three functions: (1) the reduction of hexavalent chromium to trivalent chromium, (2) precipitation of dissolved metals, (3) removal of suspended solids (metal precipitates formed in the chemical precipitation step and additional organic and inorganic solids present in the waste stream prior to precipitation). The improved metal precipitation and impurity built sludge blanket processes are designed to fulfill these functions using smaller chemical dosages, thereby reducing the quantities of sludge produced by the process.

The primary needs were to determine the operability of a SCC unit using only the metal ion impurities in the wastewater feed and the amount of iron added during hexavalent chromium reduction to form the blanket. To provide this operability assessment, blanket stability must be assured, at commercially useful flow rates and with varying IWTP feed composition, and the toxic metals must be removed to acceptable levels. Initial startup and pilot plant operation used baseline conditions with excess ferrous sulfate to provide the SCC blanket/solids. This provided both the operating stability and direct comparison to the full-scale SCC performance. The data that were needed to make the operability assessment included the following process parameters:

Control parameters:

1. Feed flow rate
2. pH
3. Blanket depth
4. Blanket solids recycle rate
5. Solids and water residence times (controlled by 1, 2 and 6)
6. Type and amounts of chemical additions (ferrous sulfate and proposed chemistries).

Measured parameters:

1. Feed composition
2. Treated water composition
3. Blanket stability.

Of the parameters above, the pH controller set point for mix tank #2 was set at 8.9 +/- 0.2 using sodium hydroxide. Borax was also tried for a test period to help control pH since it acts as a buffer at pH 8.9. Polishing chemical additions were none, ISX and phosphate.

B. EQUIPMENT CONFIGURATION AND CHEMICALS

1. Equipment Configuration

The pilot process continuously treated south equalization basin effluent. This process included three main chemical addition steps (3 mixing tanks) followed by clarification using a SCC (see Figure 23). The SCC unit was designed for a 2.5 gpm flow rate and was specially assembled for this application. The test equipment included the following components:

a. Feed Pump. The feed pump had a maximum capacity of 4 gpm. The wastewater feed rate was regulated at the desired flow rate by a control valve. A flow meter provided the signal to this control valve.

b. Chemical Addition System. The chemicals used for wastewater treatment were stored in 55-gallon polypropylene drums with covers. Metering pumps, located on the covers of the chemical storage/feed drums, were monitored and controlled by the computer control system. The pump flow rates were checked by changing the flow settings and measuring the actual flow produced by the pump.

The ferrous sulfate/sulfuric acid addition and the pH adjustment stages (mixing tanks 1 and 2) each had good mixing, with a liquid volume of 75 gal to provide a 30 minute residence time at the nominal feed flow rate of 2.5 gpm. The sodium hydroxide addition controlled the pH in mix tank #2. The other chemical feed pumps were operated manually to feed a constant amount of chemical to the pilot plant based on the wastewater feed rate and specified test conditions.

The final stage chemical addition (mixing tank 3) had good overhead mixing, with a tank volume of 50 gallons. A level sensor was used to maintain the liquid level in the tank, which provided a 15- to 20-minute residence time.

c. Solids Contact Clarifier. The solids contact clarifier was designed for 0.1 gal/min/ft² rise rate (hydraulic loading = flow rate divided by maximal cross sectional area for flow) and a liquid retention time of 13 hours. A schematic of the SCC is given in Figure 24. The unit included a flocculation chamber (for floc growth and coagulation through solids contacting and mixing) at the liquid inlet. The SCC was an up-flow inverted cone design similar in geometry to that of the full-scale SCC in current use at OC-ALC. The SCC had a rake for folding the blanket and removal of the sludge solids, an overflow weir and collection channel, a weir to hold back floating materials, a sludge recycle draw, and a recycle inlet allowing mixing with the influent. Influent to the SCC was through a diffuser (in-line static mixer) that also mixed the recycle stream and the polymer.

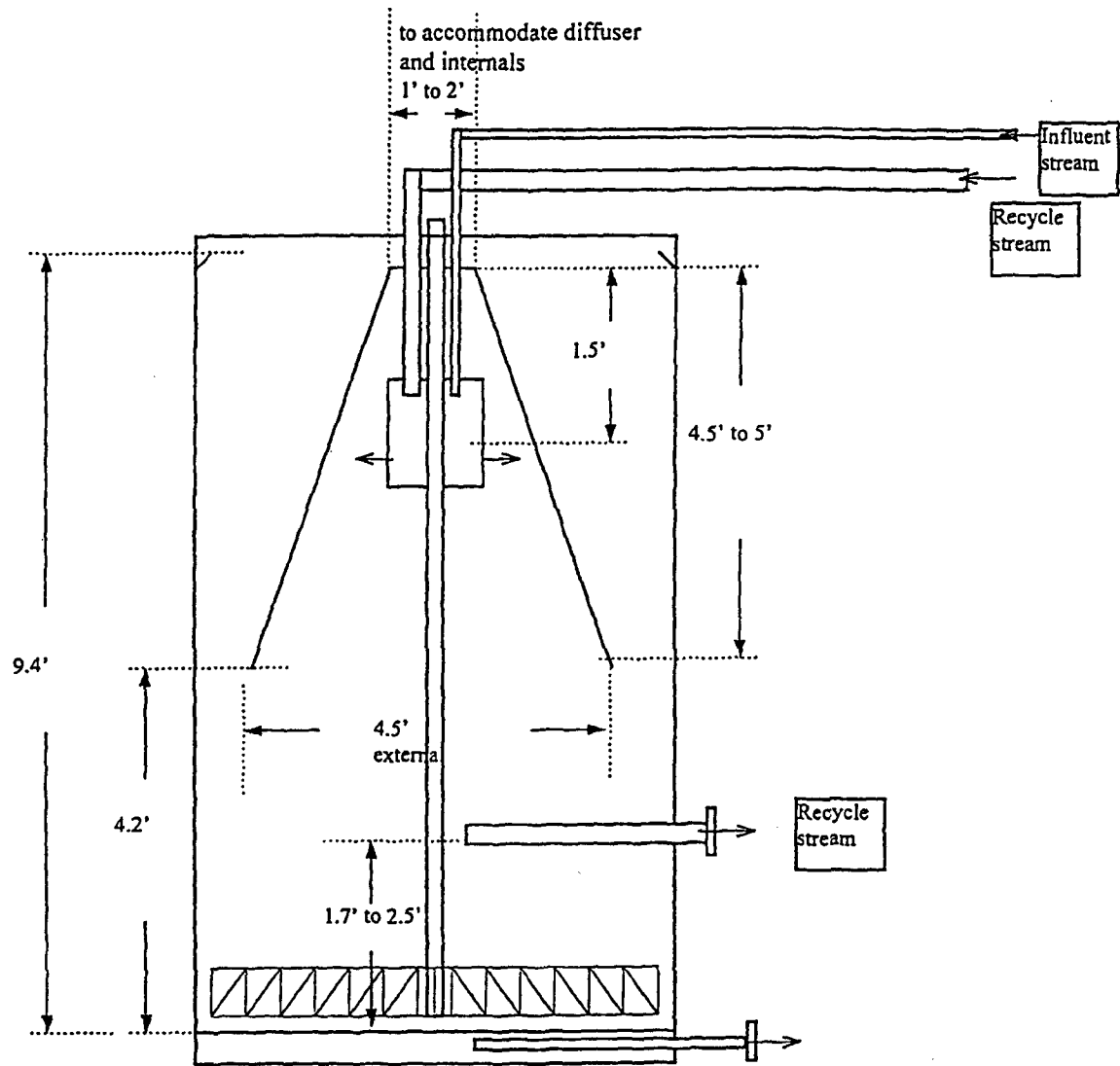


Figure 24. Schematic Drawing of the SCC.

As designed, the source for recycled SCC sludge was a pipe located 2 feet from the bottom of the SCC. During startup, the sludge compacted as quickly as it was generated, as evidenced by the solids going into the SCC, the water produced, and the lack of sludge blanket depth increase. To start sludge recycle and to reduce sludge blanket compaction, the sludge recycle source was changed from the original pipe to the SCC sludge discharge pipe located at the bottom of the SCC.

This sludge recycle change raised the sludge blanket depth but did not improve the clarity of the water or increase the size of the flocs in the SCC. Increasing the amount of sludge recycle actually increased the turbidity of the water leaving the SCC. It was noted that, in the pilot unit, the SCC did not have the same degree of mixing in the center well as did the full-scale SCC. To increase the mixing of the recycled sludge in the pilot unit to correlate better with the full-scale SCC, the sludge recycle sent to the static mixer was moved to mixing tank 3. This provided more extensive mixing of the recycled sludge with the newly formed flocs. This improved the water turbidity. The amount of sludge recycle was 600 mL every 100 seconds into mix tank 3. The solids content of the recycled sludge was found to range from 5 to 6 percent solids.

2. Contaminated Water Feed

The feed water for the pilot testing was withdrawn from and returned to the south equalization basin by means of a strained intake placed in a position near the surface of the equalization basin that avoided entrainment of tank bottom sludge or floaters. Table 14 summarizes the average pilot plant influent and effluent contaminant concentrations. TSS is important even though the pilot plant did not discharge to the IWTP plant effluent. TSS was used to estimate sludge generation rate. The sludge generation rate was low enough that no sludge needed to be purged from the SCC once the blanket was formed using high ferrous sulfate addition levels.

3. Chemical Additives

Chemical additives were evaluated for their potential to reduce the amount of metal hydroxide sludge generated. They were also evaluated for their performance in maintaining or improving the SCC performance as measured by (1) the degree of removal of toxic metal

contaminants and suspended solids, (2) improved pH control/operability, and (3) by the physical behavior of the blanket in the SCC.

In all cases the chemical additive flow rate is very small relative to the feed water flow of 2.5 gpm. Therefore, small pumps and good mixing were needed during the chemical addition tests. Chemical additives were diluted to facilitate quantitative measurements of additions, and to avoid mixing problems due to large density differences or due to the use of solid additives.

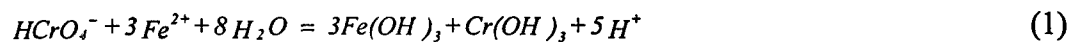
TABLE 14. PILOT PLANT INFLUENT AND EFFLUENT METAL CONCENTRATIONS.

Toxic Metal	Average^a Influent Concentration (ppb)	Pilot Plant Average Effluent^a Concentration (ppb)
Cr	8,172	276
Pb	4.5	ND ^b
Ni	1,126	54
Cd	1,687	47
Cu	24	3
Zn	112	18
Total suspended solids (TSS)	60,500	39,500

^a Average based on 10 samples taken during pilot plant operations, October 1, 1997 – November 19, 1997. Influent samples include spike of chromium, nickel, and cadmium.

^b ND = None detected.

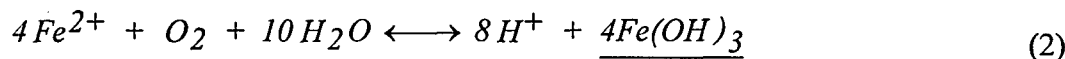
a. Ferrous Sulfate Heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) Additive. Ferrous sulfate reduction of hexavalent chromium utilizes the transfer of electrons from divalent ferrous ions to the hexavalent chromium ion. Thus, iron(II) is oxidized to trivalent ferric ions while reducing the chromium(VI) to trivalent chromium(III) ions according to reaction 1.



Ferrous sulfate was added at the hexavalent chromium reduction tank. Residence times were about 30 minutes (designed as currently used in the IWTP).

In order to prevent precipitation of Fe^{2+} as $\text{Fe}(\text{OH})_2$, the pH in mixing basin 1 was maintained at 6 ± 0.5 . Therefore, a small amount of sulfuric acid was added with the ferrous sulfate to maintain the pH of the feed stream. This acid also helps prevent the oxidation of ferrous ion to ferric ion in the feed tank. Note that only a very small amount of this acid was required to achieve the required pH control.

Excess ferrous sulfate is naturally removed by air oxidation (Reaction 2) as the fluid flows through the mixing tanks, piping and the SCC.



b. Borax (Sodium Tetraborate Decahydrate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) Additive. A common problem in IWTP operations is pH control. This pH control is a particular concern in metal hydroxide precipitation steps since toxic metal resolubilization occurs if the pH is just several tenths above or below the set point, $\text{pH } 8.9 \pm 0.2$ in the case of trivalent chromium. Moreover, unless a buffer is already present in the wastewater, the target precipitation pH is difficult to control since it represents an equivalence point, i.e., the point at which exactly three hydroxide ions per trivalent metal ion (i.e., Cr^{3+}) exist, or two per divalent ion (i.e., Cu^{2+} , Cd^{2+} , Ni^{2+} , etc.). Therefore, small additions of acid or base significantly change the ratio $[\text{M}(\text{OH})_x] / [\text{M}(\text{OH})_{x \pm 1}^{\pm}]$, since the $[\text{M}(\text{OH})_{x \pm 1}^{\pm}]$ is so small, <100 ppb.

Currently, good pH control in IWTP operations is accomplished via operator training, use of dilute caustic solutions, and careful monitoring with semiautomatic control. It is known that, as the SCC blanket ages, additional pH fluctuations can occur, usually downwards, which can again cause resolubilization of toxic metals at low but problem levels. Therefore, the use of borax as a buffer for pH control at 8.9 was tested to determine if it caused any adverse effects on the process, such as, turbidity problems or increased metal ion solubilization.

Borax has a pH buffering effect close to the optimum pH for metal hydroxide precipitation, 8.9 ± 0.2 . Other wastewater components, such as bicarbonate and phosphate do not buffer at this pH. Borax is not used in current operations and, therefore, was not used in the baseline test. Borax is believed to have no adverse effect on the aerobic bacteria used in biotreatment, especially at the low concentrations (4-12 ppm) added during treatment. The amount of borax used was minimized to reduce chemical cost and avoid excess TDS. The greater the borax concentration, the stronger the pH buffering effect. Borax was added at the pH adjustment tank (mix tank 2).

c. Sodium Hydroxide Additive. Sodium hydroxide is currently used at many IWTPs for pH adjustment and to supply the hydroxide ion needed for precipitating toxic metal ions as solid hydroxides. It was used for this same purpose in the pilot tests. Sodium hydroxide was added at the pH adjustment tank to maintain pH values of 8.9 ± 0.2 . Residence times at nominal flow rates were in the 30-minute range, as currently used in the IWTP.

d. Sodium Phosphate, Dibasic (Na_2HPO_4) Additive. Chromium(III) hydroxide solid is amphoteic and hence exhibits a narrow pH range, $\sim 8.9 \pm 0.2$ over which it has minimal solubility. Traditional polishing agents such as sulfides and polymeric sulfur donors do not bond with trivalent chromium because of the very slow rate (days to weeks depending on temperature) at which it reacts. Chromium(III) salts with sulfate, carbonate, chloride, carboxylates, and others are soluble, so removal of chromium by precipitation is less effective in the presence of these anions. Like other trivalent metal ions, chromium(III) forms highly insoluble phosphates ($\text{pK}_{\text{sp}}^{\text{CrPO}_4} = 17-23$ depending on morphology). These salts exhibit a larger pH range of low solubility. Importantly, at $\text{pH} > 8.5$ ferric phosphate does not form because its hydroxide precipitate is less soluble. Hence, at pH 8.9 phosphate is expected to exhibit selectivity for chromium(III) over

ferric iron. This selectivity reduces the amount of phosphate addition needed to effect chromium removal, and therefore also reduces the operating costs, TDS and sludge volume.

Ortho-phosphate ion, added as dibasic sodium phosphate hydrate, forms highly insoluble precipitates with trivalent chromium and iron(III) at pH near 8.5. This property makes it an attractive polishing agent for trivalent metals. If chromium elimination is insufficient, then sodium phosphate could be added to polish the effluent.

The baseline test and the initial borax test did not utilize phosphates. The phosphate tests used (1) 105 percent of stoichiometric quantities of phosphate relative to the total Cr in the influent; and (2) the lower concentration, at 20 percent of the total stoichiometric requirement. The tests determined that phosphate was effective in improving the elimination of Cr^{3+} . Cr levels in the SCC effluent were determined by ICAP analysis. The need for phosphate polishing was decided based on the Cr concentration in excess of NPDES limits. Na_2HPO_4 , when needed, was added to the treated water just prior to the point where it enters the SCC (mixing tank 3).

e. Insoluble Starch Xanthate (ISX) Additive. ISX is a solid with sulfur substituted sites that can bind certain mono and divalent base and noble metals and thereby remove them down to very low concentrations. It is used as a polishing agent to reduce toxic metals such as Cu, Ni, Cd, and Ag.

ISX was not used in the baseline tests or in the borax pH adjustment test. ISX was added in two test runs to eliminate the above metals (1) at 100 percent of stoichiometry and (2) at 20 percent of stoichiometry. ISX captures these metals, especially Cd, as the blanket ages. ISX also is useful for removing chelated metals. Note that ISX is not effective for Cr^{3+} , Fe^{3+} , Ca^{2+} , Mg^{+} , Na^{+} , or Al^{3+} removal. The use of ISX should be minimized as it will contribute to sludge mass and process cost; process economics limit ISX addition rates to no more than 20 percent of the total divalent metal ion concentrations in the influent. ISX was added directly to mixing tank 3. Stock ISX needs to be kept refrigerated where it has a shelf life of about six months. ISX must never be acidified to under pH 7 or flammable, noxious CS_2 fumes will result.

f. Betz 1195, Betz 1120, and Drew 270 Polymer Flocculants. Cationic (Drew 270, Betz 1120) and anionic (Betz 1195) polymer flocculants and coagulants are charged, long chain, water soluble polymers that bind suspended particles together into larger aggregates, or flocs that settle more readily than small particles.

Betz 1195 and Betz 1120 polymer flocculants are in use at the OC-ALC IWTP to aid in floc formation and thickening, so these flocculants were used in baseline testing. Visual observations were made during pilot plant operations. Using standard "jar tests", the polymer addition rate was adjusted until nice looking flocs were formed. Nice flocs were defined to be well-formed particles of solids, over 1/32-inch in size.

4. SCC Blanket Stability

The function of the solids contact clarifier is the removal of suspended solids from the wastewater stream. The operating principle of contact clarification is the aggregation of small-suspended particles with larger particles by orthokinetic flocculation. The small particles and the metal hydroxide colloids in the influent stream are contacted with larger solids that are circulating in a sludge blanket. The influent is thoroughly mixed with a recycled portion of the blanket, which then flows through the blanket of suspended particles, thus providing a large chemically reactive surface area that stimulates the attachment of small particulates and colloids to the larger particles. The SCC blanket provides the small particles with an opportunity to grow at a much higher rate than the natural rate of discrete particle nucleation and growth in dilute solids suspensions. For good collection, sludge blanket needs to be uniformly distributed and sufficiently large and thick (high solids content) to allow complete elimination of suspended particles. The wastewater flow through the blanket must be sufficiently slow (i.e., low velocity) to allow time for contacting, prevent wastewater bypass of the blanket by channeling, and avoid entrainment of blanket solids. The age of the particles affects their absorption capacity, so older particles must be removed. This purge of the blanket is performed by removing the largest sludge particles from the bottom of the SCC under the rake.

C. SCC PILOT PLANT TEST RESULTS

The tests proceeded from a potable water run for calibration and leak detection, through initiation of the blanket and then to the test sequences. The test program varied the chemistry by changing the chemical addition rates.

1. Setup

The pilot plant equipment was assembled and checked for operability and calibration. The SCC and chemical addition system were tested for leaks and proper function of the pumps by using potable water feed (to prevent contamination of the equipment that may require service). The chemical storage/feed tanks were filled with water and the metering pumps operated at flow rates in the operating range. Flowmeters were calibrated by measuring the volume discharge collected over known operation times. The main line pumps were run at their nominal flow rate, the SCC was filled, and the overflow allowed to run for a few hours after the metering pumps were checked. The system was closely inspected to locate any leaks, control system malfunctions, flow rate instabilities, or tank overflows.

2. Startup

Start up of the process was intended to build the iron hydroxide sludge blanket and properly fill the tanks and the SCC.

3. Creation of the Initial Sludge Blanket for the Baseline Test

The initial sludge blanket in the SCC was formed by feeding excess ferrous sulfate to the unit. The sludge from the IWTP was not used because it is a sulfide sludge, instead of a hydroxide sludge. The sludge blanket accumulated to the desired level of 4 feet over several weeks of operation. There were several interruptions in operation over this period. The most significant interruption was occasioned by the need to replace the PLC touch control panel.

After calibration and pilot plant shakedown were completed, wastewater flow to the pilot plant was started. Adding high amounts of ferrous sulfate to this wastewater formed the sludge blanket. The total suspended solids into the pilot plant averaged 23 milligrams per liter. The wastewater feed rate was 2.4 gpm (9.08 liters per minute). This would result in 209 mg/min of TSS flow to the SCC. The volume of the SCC is about 2000 gallons. The sludge blanket depth needed to be at least 4 feet out of the total 10-foot height of the SCC. If the solids content of the sludge were 5 percent, then 333 pounds of solids would be needed to form a 4-foot-deep blanket. This would take 505 days at a 209 mg/min TSS feedrate.

When a sludge blanket started to form, the recycle point was switched from the 2-foot level to the bottom to allow for better sludge recycle. The bottom was thicker though the sludge level was not increasing very quickly. It appeared the sludge was compacting as fast as it was forming. The sludge discharge line was valved off to prevent the possibility of any of the sludge being pumped out while the sludge blanket was accumulating. During the sludge blanket build up it was observed that the higher the sludge recycle rate the higher the effluent water turbidity from the SCC. The lowest turbidity was achieved while the SCC was operated as only a clarifier with no sludge recycle.

A Streaming Current Detector (SCD) was installed for a period of time during pilot plant operation to evaluate its benefit in determining polymer dosages needed to form and maintain good flocs for SCC operation. The SCD monitored the wastewater in mixing tank 3. When the cationic polymer was increased, the SCD reading increased. When the cationic polymer was decreased or the anionic polymer was increased, the SCD reading decreased. The anionic polymer, Betz 1195, had a much stronger charge than did the cationic polymer, Drew 270. When good flocs were being formed, the SCD reading was noted. As time progressed, the SCD reading would change with changes in the influent wastewater. The flocs would still be forming well. If the polymer feedrates were adjusted to bring the SCD reading back to where it was before, the flocs would stop forming as well. In an operation such as the OC-ALC IWTP, the SCD may not be practical. Changes in the wastewater properties affect the SCD reading, while not affecting the floc formation performance. However, the SCD provides an indication of changes in the IWTP that might require operator attention.

Chromium and other metal concentrations were found to be low in the feed water to the pilot plant. Therefore, a spiking solution was used to increase the concentration of hexavalent chromium, nickel, and cadmium. Potassium dichromate, nickel sulfate and cadmium sulfate were used to prepare the spike stock solution.

The spike solution was made by adding 972.8 grams of potassium dichromate ($K_2Cr_2O_7$), 159.4 grams cadmium sulfate ($CdSO_4$) and 226.1 grams nickel sulfate ($NiSO_4$) to 50 gallons of water. This solution was metered into the pilot plant feed at 20 mL/min resulting in a minimum feed concentration of 4 mg/L of chromium, 1 mg/L of cadmium and 1 mg/L of nickel. The chromium was added as hexavalent chromium. The readings by the Hach test kits of the influent wastewater concentrations after spike addition were 0.6 to 0.9 mg/L hexavalent chromium. This indicates that something in the wastewater was reducing most of the chromium before any pilot plant operation. The pilot plant operation did reduce the remaining hexavalent chromium. The chromium of the spike does show up in the total chromium analysis of the influent wastewater. The range for total chromium in the equalization basin for a week in July was 0.6 to 0.7 mg/L, as shown in the data in Table 15. The chromium concentration of the pilot plant influent after the spike addition ranged from 2.1 to 15.8 mg/L. The chromium levels varied with time as the sample was taken from the feed sump. The spike solution was pumped into the sump at a constant rate, while the sump was emptied and filled by a pump controlled by high and low level sensors located in the sump. The total chromium pilot plant feed concentration should average 4 mg/L plus what was contained in the influent wastewater. This is based on the influent chromium concentration and the spike solution. The on/off nature of the feed sump from the high and low level sensors results in fluctuations in the feed concentration.

4. Sampling Plan

Samples were collected from the influent and effluent streams of the pilot plant for chemical and physical analyses. The influent stream was taken from the feed sump in each of the tests of the pilot SCC unit.

These samples were collected in appropriate sample containers and documented as having been decontaminated and supplied with appropriate preservatives (chemical additions and cooling, if required). Each sample was provided with a unique identifier; sample containers were appropriately labeled at the time of sample collection. After the sample was collected and

TABLE 15. SAMPLE ANALYSES OF EQUALIZATION BASIN FOR THE WEEK OF JULY 21st.

Description	Total Metals (ppb)						O&G	TSS
	Cd	Cr	Cu	Pb	Ni	Zn		
System Inlet, Monday July 21	10.4	866	19.4	10.0	39.0	89.8	6	NA
System Inlet, Tuesday July 22	9.9	698	16.5	ND	39.1	82.3	5	50
System Inlet, Wednesday July 23	11.6	675	17.5	8.2	38.8	84.9	5	60
System Inlet, Thursday July 24	10.3	613	16.4	7.5	47.9	112	4	38
System Inlet, Friday July 25	11.7	682	17.4	6.8	49.0	113	ND	57
	Soluble Metals (ppb)							
System Inlet Tuesday July 22	ND	49.6	5.75	ND	22.0	47.2		
System Inlet Wednesday July 23	ND	33.4	ND	ND	24.4	119		
System Inlet Thursday July 24	ND	50.8	1.1	ND	18.4	60.3		
System Inlet Friday July 25	1.5	184	3.8	ND	36.9	74.7		

the container labeled, the samples were transported to the analytical laboratory (AnaLab). The analyses for hexavalent chromium (Cr), ferrous iron, and turbidity were conducted on site within 1 hour of sample collection.

5. Sample Analysis

Samples were withdrawn from a flushed tap on the pilot SCC system for effluent and from the feed sump for influent at the initiation of and during each test run. Effluent hexavalent chromium and ferrous iron concentrations, and turbidity, were measured on site as frequently as practicable to determine the effectiveness of the reduction process and the effectiveness of the blanket in solids capture. Total suspended solids tests were conducted when metals were analyzed.

The hexavalent chromium levels were checked with Hach test kits. The kits use a colorimetric complexing reagent with an electronic colorimetric detector. These kits have a maximum concentration limit of 1 mg/L, which requires dilution of concentrated samples to keep the chromium under 1 mg/L. Only once did the influent wastewater concentration approach or exceed 1 mg/L. The kits can have problems with iron interference: the presence of iron causes a false positive response. No indication of this interference was evident during these tests. During testing and during the ferrous reduction operation, the kits were used on the contents of mix tank 3 before the iron was settled out of the solution. Little to no hexavalent chromium was ever detected at mix tank 3 or at the outlet of the SCC. During the very end of the pilot plant operation, all ferrous sulfate feed was stopped while pH control was continued. Chromium(VI) was found at the sump, mix tank 1, mix tank 2, mix tank 3, and at the outlet of the SCC when there was no sludge recycle, even to mix tank 3. As soon as sludge recycle was started to mix tank 3, the hexavalent chromium concentration went to zero (<10 ppb) after 10 minutes at a pH of 8.5.

6. Data Processing and Procedures

Data were collected before, during, and after each Test Run and recorded. Sampling was conducted in accordance with the sampling plan. All samples were marked with the sample date and time, run conditions, where the sample was taken, the preservation method used, and what analysis was required. An actual data sheet is shown in Figure 25.

DATE	17 Nov 77	SLUDGE BLANKET DEPTH	TIME	3.0"	TIME	3'
INFLUENT CHROME (IWT PLOGS)	TIME	TIME	TIME	TIME		
EFFLUENT CHROME	TIME	0.00	TIME	0.00		
INFLUENT	TSS		TAKEN	METALS		TAKEN
EFFLUENT	TSS		TAKEN	METALS		TAKEN
BLANKET	TSS		TAKEN			
INFLUENT TURBIDITY	109	TIME	1430	TIME		
EFFLUENT TURBIDITY	94	TIME	46 @ 1450	TIME		
INFLUENT OBSERVATIONS	yellow m.w. cr ⁺⁺ → 0.49 @ 0807 0.64 @ 1450					
EFFLUENT OBSERVATIONS	Bundley					
TANK 1 OBSERVATIONS	DPA Borneo					
TANK 2 OBSERVATIONS	DPA Borneo					
TANK 3 OBSERVATIONS	Black - good Fluc. 35.3 SCD @ 1430					
BLANKET OBSERVATIONS	Black - some chuffing. 1530 3'					
CHEMICAL FEED DRUM ACTIVITY						
TIME	DRUM	LEVEL OF DRUM	AMOUNT OF CHEICAL ADDED			
1430	FeSO ₄	37				
1430	Spike	30				
1430	H ₂ O ₂	45				
1430	270	31				
1430	1195	31				
1430	Starch	20	added 1 lb H ₂ SO ₄ filled to 50 galls			
NOTES	Had Cold Damage on week - PIC Bushing Cracked					
On influent line to SCL. Some leakage all contained in						
Blue SLD - Repaired Sunday 16 Nov - Estimated Damage Easily						
Sunday morning.						
at 4:00/1 (1600) started feed starch + phosphate at 50%						

Figure 25. Example of Daily Log Report.

7. Baseline Test

After the sludge blanket was formed, the ferrous sulfate feed rate was set at 22 mL/min. The ferrous sulfate concentration was 8700 mg/L in the feed solution, resulting in a concentration of 21 mg/L in mix tank 1. The pH in mix tank 1 ranged from 7.1 to 7.2 (higher than the $\text{pH } 6.0 \pm 0.5$ target, indicating that the ferrous reducing agent was as $\text{Fe}(\text{OH})_2$ particulate and colloids, rather than Fe_{ag}^{2+} ion (see section 3.3.1). The pH of mix tank 2 ranged from 8.8 to 9.3 also outside of the target pH of 8.9 ± 0.2 (section 3.3.2). Plots of pH verses time are given in Figure 26a. Figure 26b shows the ferrous sulfate and the wastewater feed rates to the pilot plant. Figure 26c shows the oxidation-reduction potential (ORP) of mix tank 1. The ORP was recorded during pilot plant operation to determine if the readings provided an indication for control of the pilot plant parameters, not for actual control of the pilot unit. The final graph, Figure 26d, shows the influent and effluent hexavalent chromium levels during the baseline test period. Little to no hexavalent chromium was found in the pilot plant effluent from the SCC until October 6 and 7 (Figure 26d). The October 1 and 7 samples are from the baseline period. The cadmium, chromium and nickel were all reduced by 90 percent while copper and zinc were reduced about 80 percent. The copper and zinc were not removed as well as the other metals but were already present at low concentrations in the influent wastewater. The percent metals reduction is shown in Figure 27. The actual effluent and influent metal concentrations are shown in Figure 28; the influent levels of copper, zinc, and lead were very low, all below 100 $\mu\text{g/L}$. This was why chromium, nickel and cadmium were spiked, since they were also low in the unspiked influent.

8. Reduced Ferrous Sulfate Test

The ferrous sulfate feed rate to mix tank 1 was reduced 50 percent to 11 mL/min on October 7, 1997. This feed rate provided a ferrous sulfate concentration of 10 mg/L in mix tank 1. The operating conditions are shown graphically in Figure 29, and the actual effluent and influent metal concentrations in Figure 30. There was an interruption in operation when the feed pump stopped on October 9. The chemical feed pumps continued to feed, resulting in the pH going high in mix tank 2. It appears that the ORP also increased when the feed stopped;

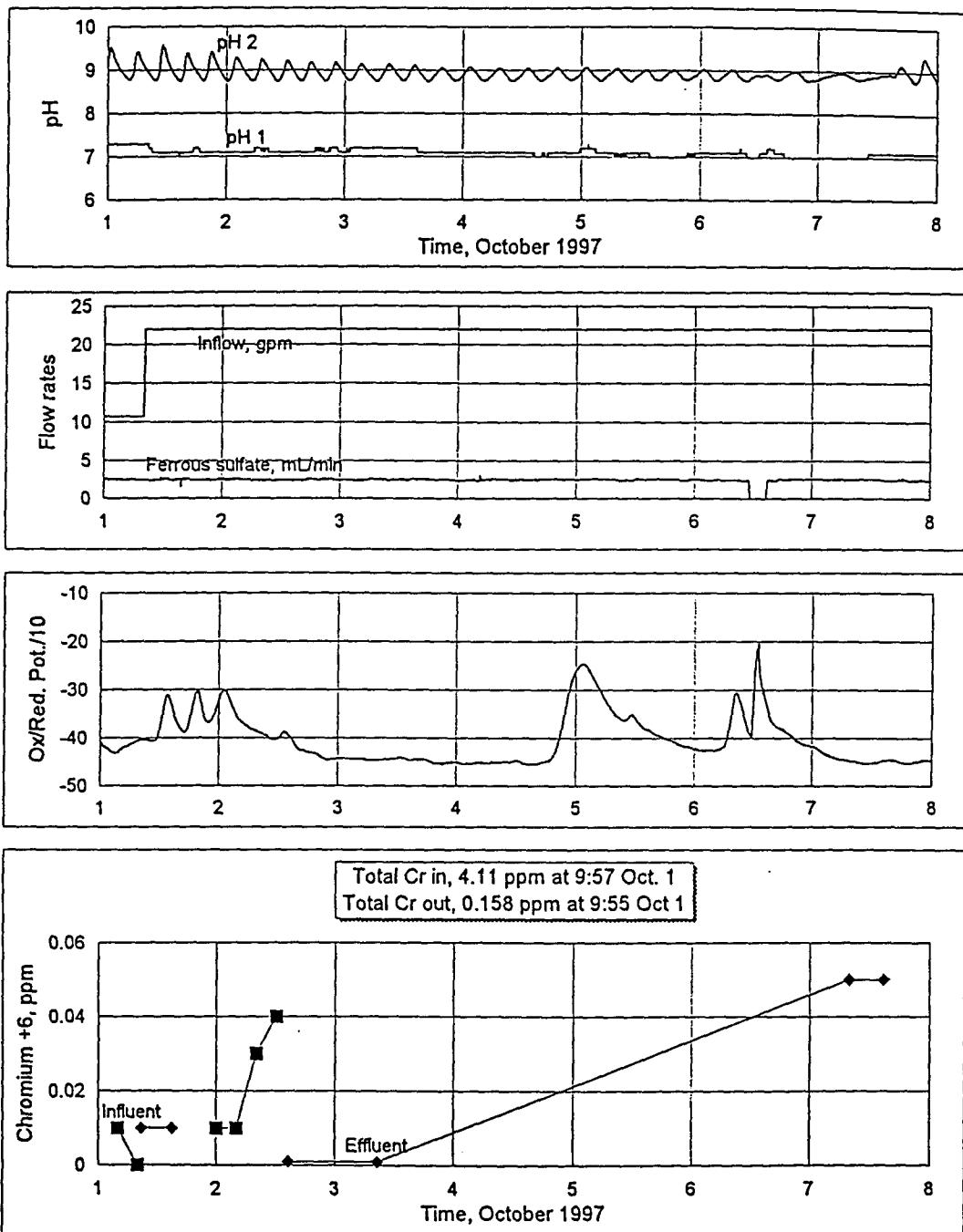


Figure 26 a,b,c,d. Baseline Operational and Analytical Data.

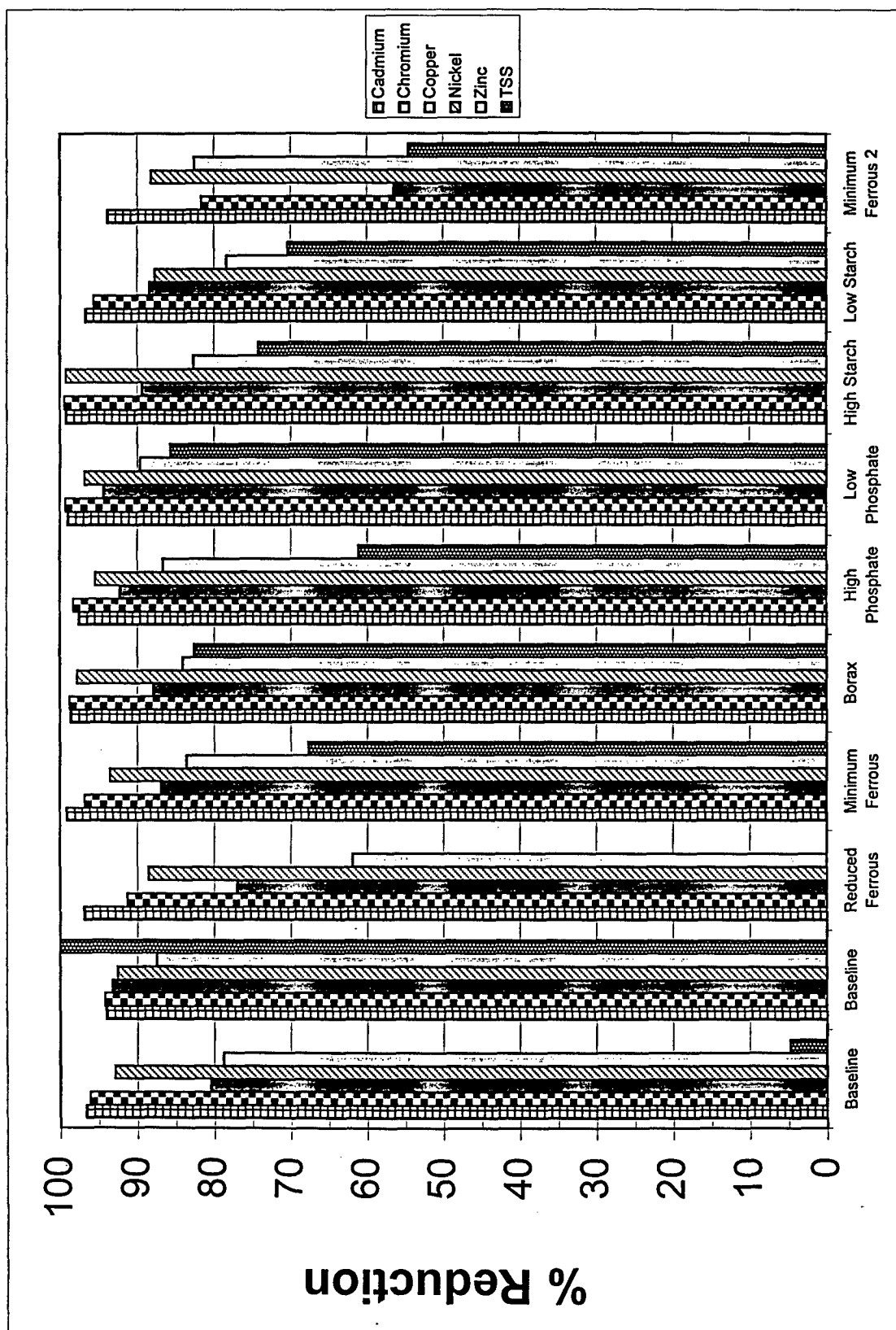


Figure 27. Percent Total Metals Reduction.

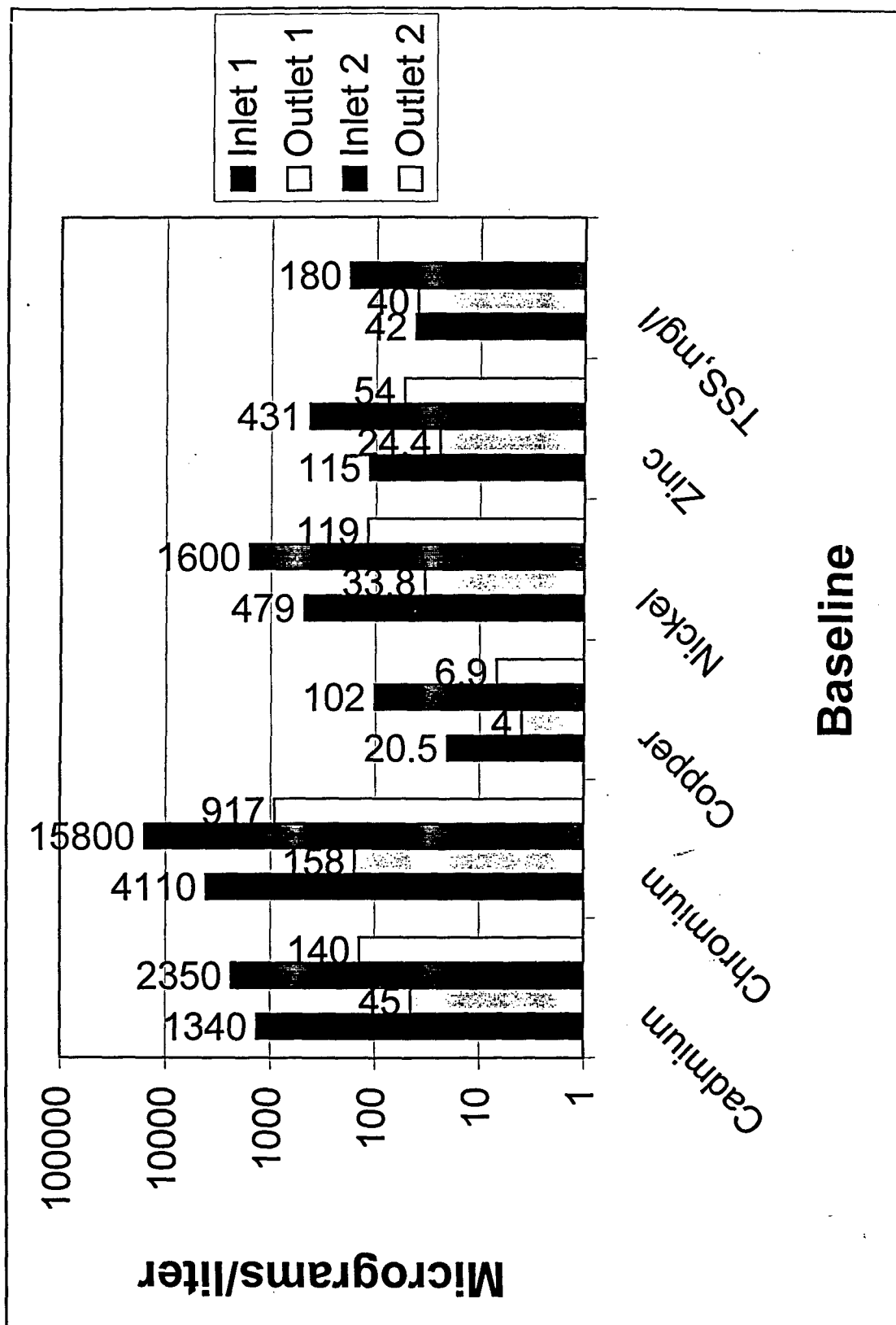


Figure 28. Baseline Metals Concentrations.

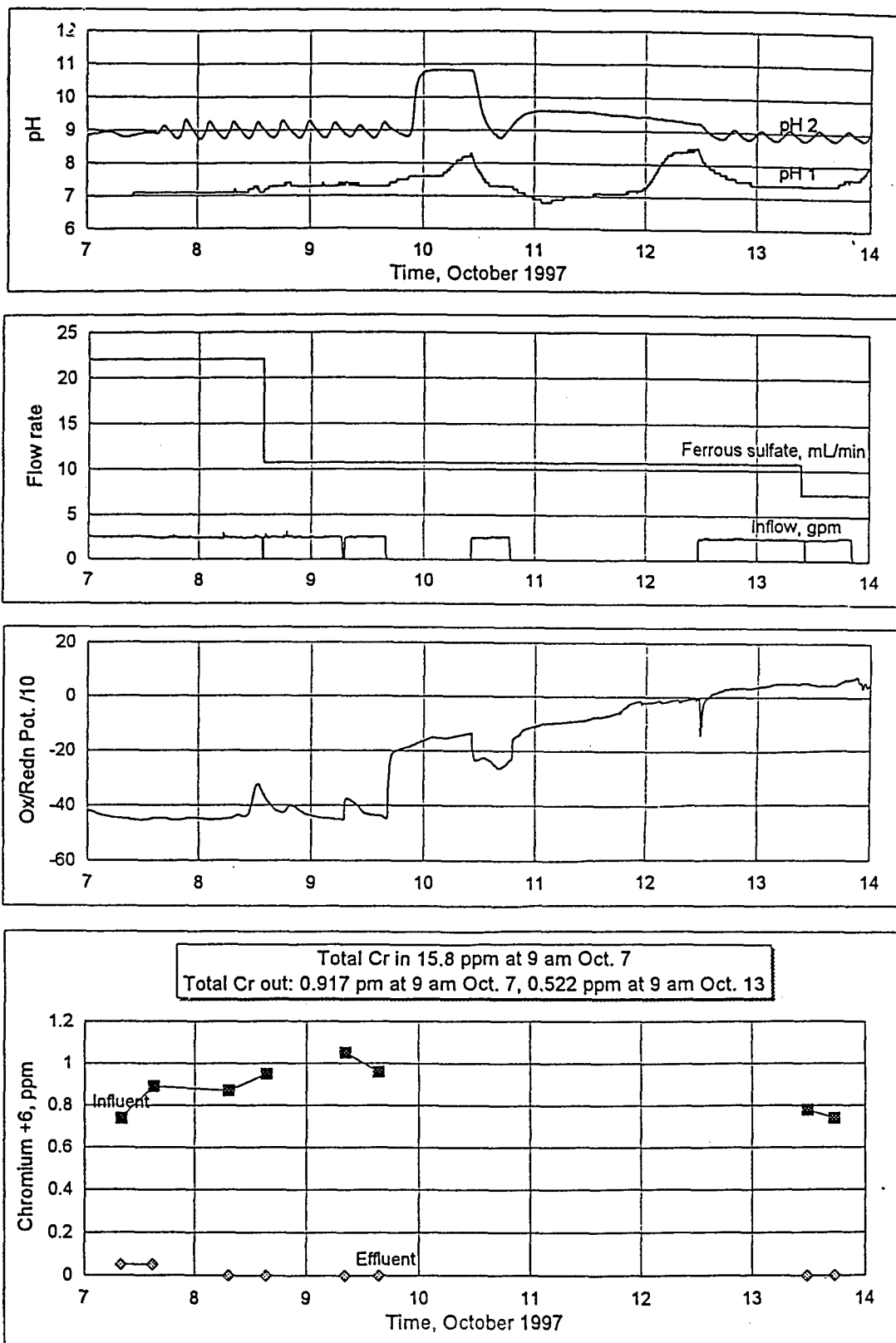


Figure 29. Reduced Ferrous Sulfate Test Operational and Analytical Data.

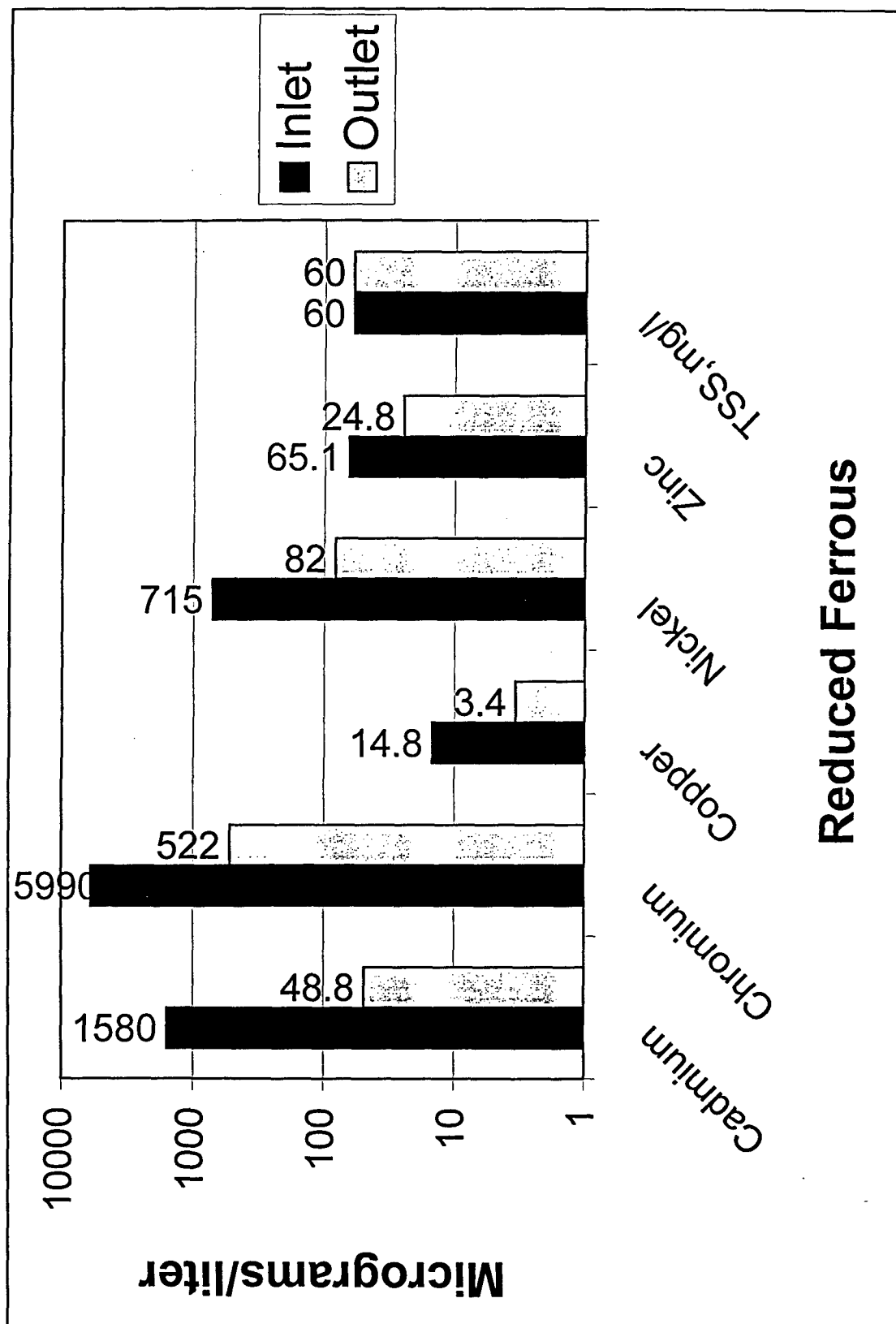


Figure 30. Reduced Ferrous Sulfate Metals Concentrations.

however, when the feed was restarted, the ORP remained elevated. Changes in the ferrous sulfate feed rate did not impact the ORP reading. This indicates that something other than the ferrous sulfate addition affected the ORP. There are many other compounds that could be impacting the ORP. These compounds include phenol, chlorine, dissolved oxygen, and chromates. Evidently, the wastewater contained a compound that has a stronger effect on the ORP than does the ferrous sulfate. This may explain the partial reduction of the spiked hexavalent chromium in the feed tank. During the reduced ferrous sulfate test period, no hexavalent chromium was detected in the SCC effluent.

9. Minimum Ferrous Sulfate Test

The next test was to determine the minimum ferrous sulfate feed rate needed to reduce the hexavalent chromium. The ferrous sulfate feed rate was reduced until hexavalent chromium was detected at mix tank 3 and then increased slightly until the hexavalent chromium concentration returned to zero. The feed rate adjustments and operating conditions during the minimum ferrous sulfate test are shown in Figure 31. The final ferrous sulfate feed rate was 8.5 mL/min, which gave a ferrous sulfate concentration of 8 mg/L in mix tank 1. The graphs show another feed stoppage and the variability of the ORP. The pH control was smoothest when the sodium hydroxide solution was more dilute. This result confirms that pH control can be a problem in SCC process control, suggesting the use of borax if operator training is at issue. The metals removal was better than during the reduced ferrous sulfate test but the influent metal concentrations were also decreased. The pH of the solution in mix tank 1 was above 7.0 throughout this test. At this pH, the added ferrous sulfate would exist as ferrous hydroxide particulate and colloids. This change is expected to result in slower hexavalent chromium reduction rates. The metal analysis results are shown graphically in Figure 32.

10. Borax Test

Borax was added to mix tank 2 in this test. The feed solution was 4 pounds of anhydrous sodium tetraborate mixed with 50 gallons of water. As expected, based on the percent metals reduction data, borax did not significantly enhance or hinder metals removal. The operational data are shown in Figure 33. For strict pH control, better pH controller tuning and/or use of more dilute caustic (see above) would be the cheaper alternative. However, if operator

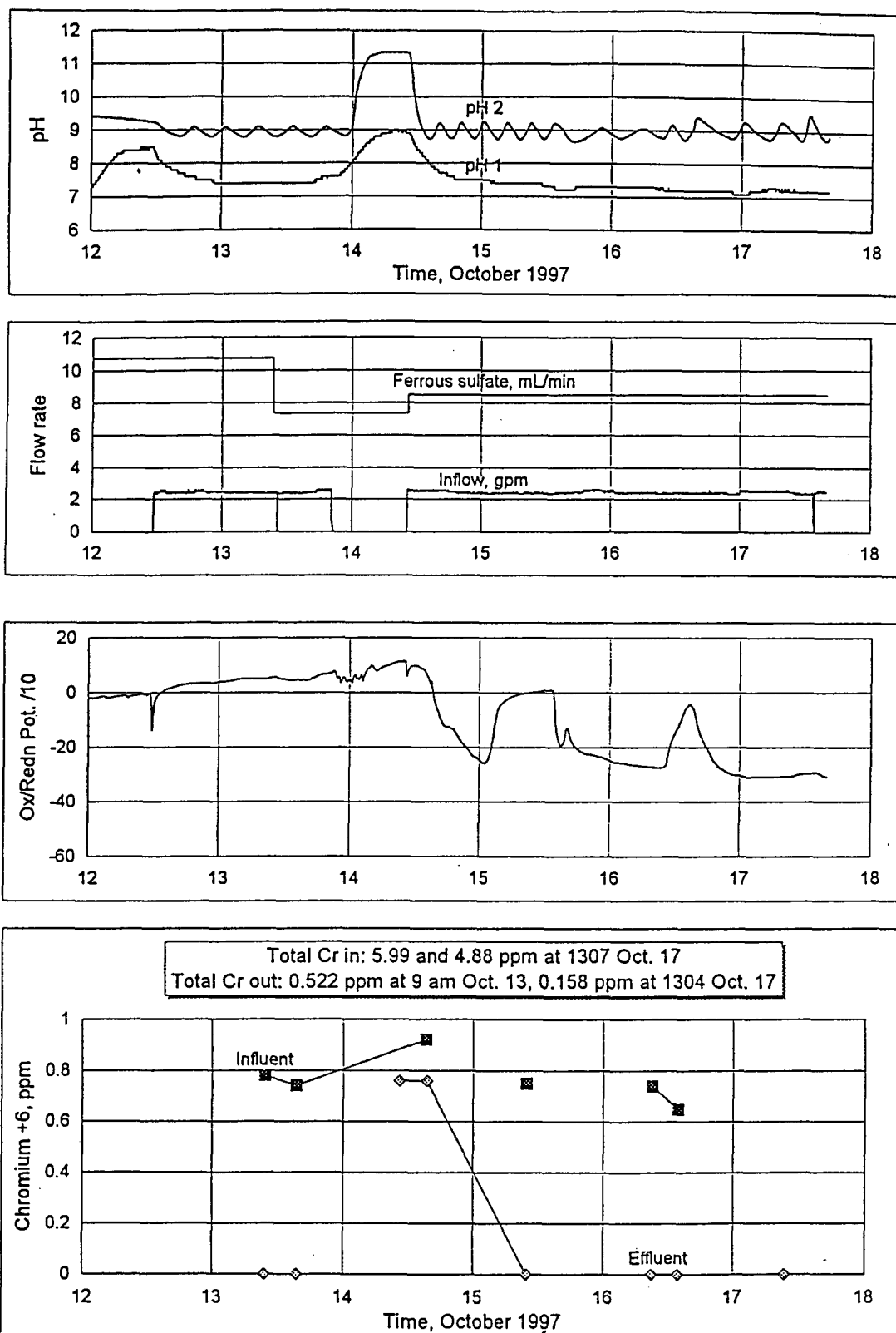


Figure 31. Minimum Ferrous Sulfate Test Operational and Analytical Data.

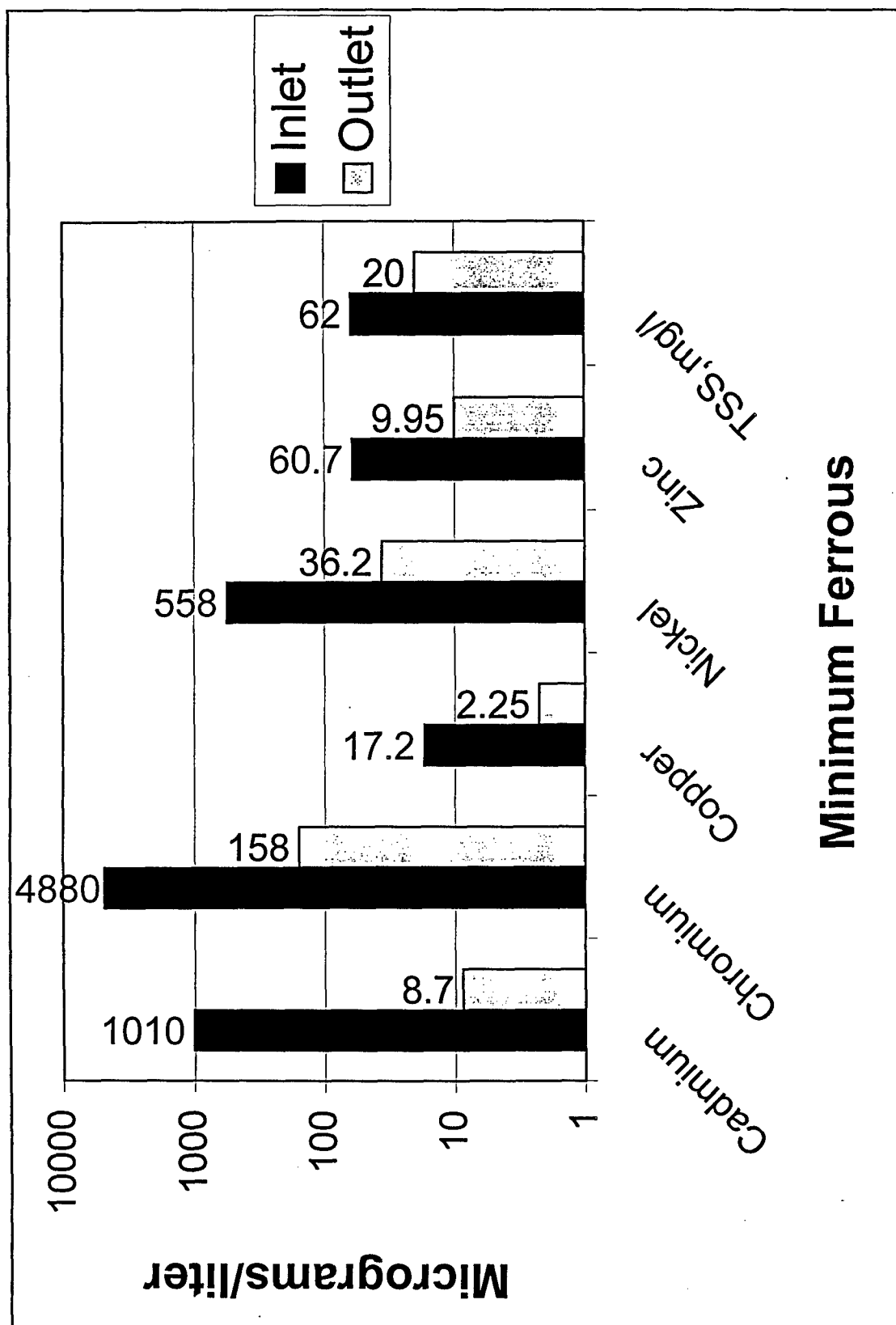


Figure 32. Minimum Ferrous Sulfate Test Metals Concentrations.

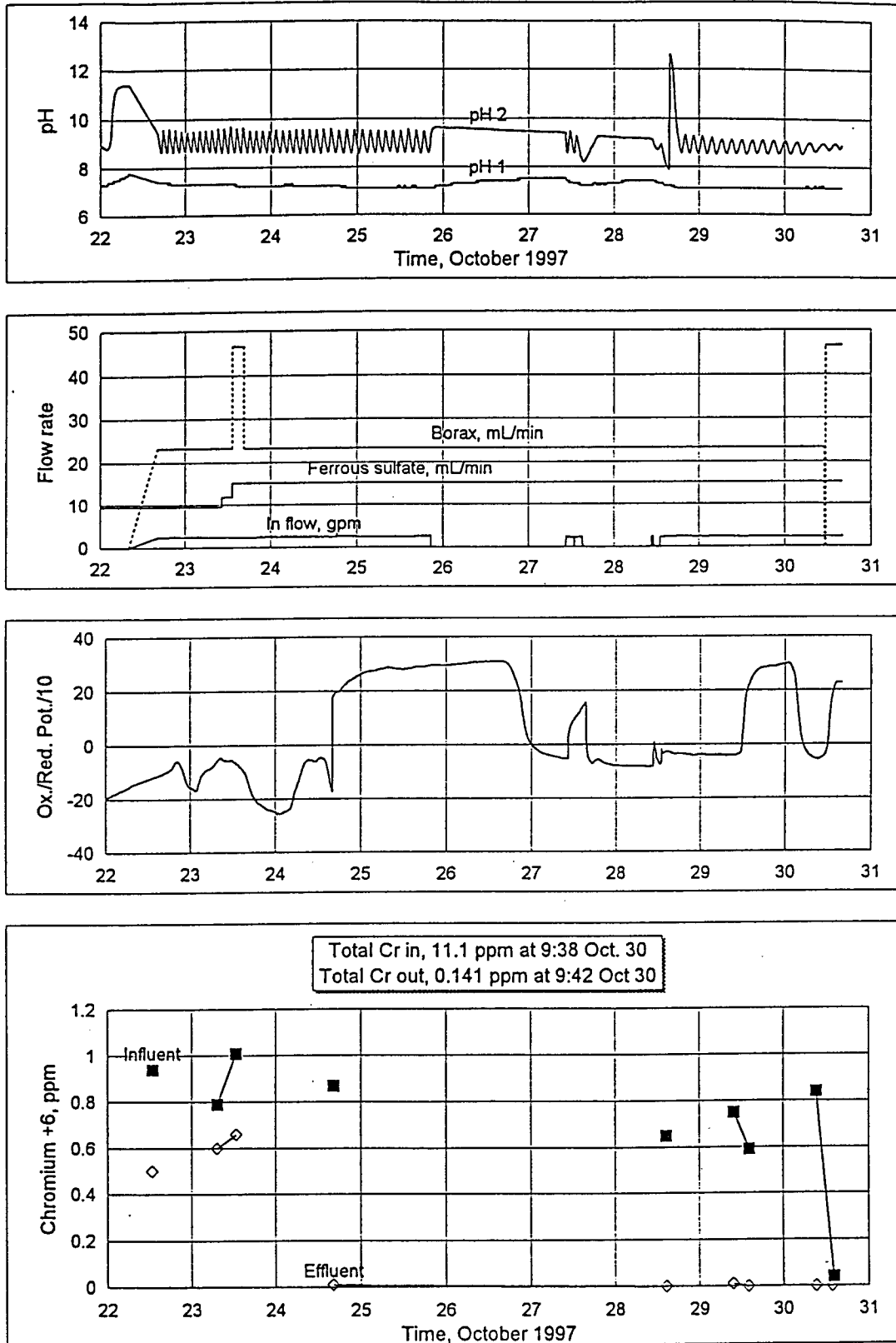


Figure 33. Borax Addition Test Operational and Analytical Data.

training and consistency is an issue, then the use of borax buffer may be justified. The metal analysis results are shown graphically in Figure 34.

11. Phosphate Test

Sodium phosphate was tested to determine whether additional trivalent chromium removal could be achieved. The phosphate feed solution was made from 1.15 pounds of sodium phosphate per 55 gallons of water. The sodium phosphate was added to mixing basin 3. The operating conditions for this test are shown graphically in Figure 35. By looking at the effluent total chromium levels in Figure 27 for the phosphate testing it can be seen that the lowest levels of total chromium were achieved during the use of sodium phosphate addition. The levels dropped to a low of 58 micrograms per liter. The levels went back up after the phosphate addition was stopped. Therefore, phosphate addition is an effective means for reducing chromium (III) levels below those achievable by pH adjustment alone. The metals analysis results are shown graphically in Figures 36 and 37.

12. Insoluble Starch Xanthate (ISX) Test

ISX, as cross-linked gel particles, is used as a polishing agent to remove certain toxic divalent metals to concentrations below those achievable with hydroxide addition alone. The ISX was added to mix tank 3. The feed solution of ISX was made from 1.15 pounds of material added to 55 gallons of water. Figure 38 graphically shows the operating conditions of the pilot plant during the ISX addition test.

The lowest concentration of nickel was achieved using the starch (see Figure 27). The highest removal percentage for cadmium and nickel were also achieved using the starch. The highest concentration tested was needed to achieve these results. When the starch feed rate was decreased, the effluent metals concentrations increased. The high ISX concentration was 6 mg/L and the low ISX concentration was 3 mg/L. The ISX may have had reduced effectiveness due to the sludge recycle to mix tank 3, as it could have been easily consumed by the large excess of contaminants present in the sludge. The metal analysis results are shown graphically in Figures 39 and 40.

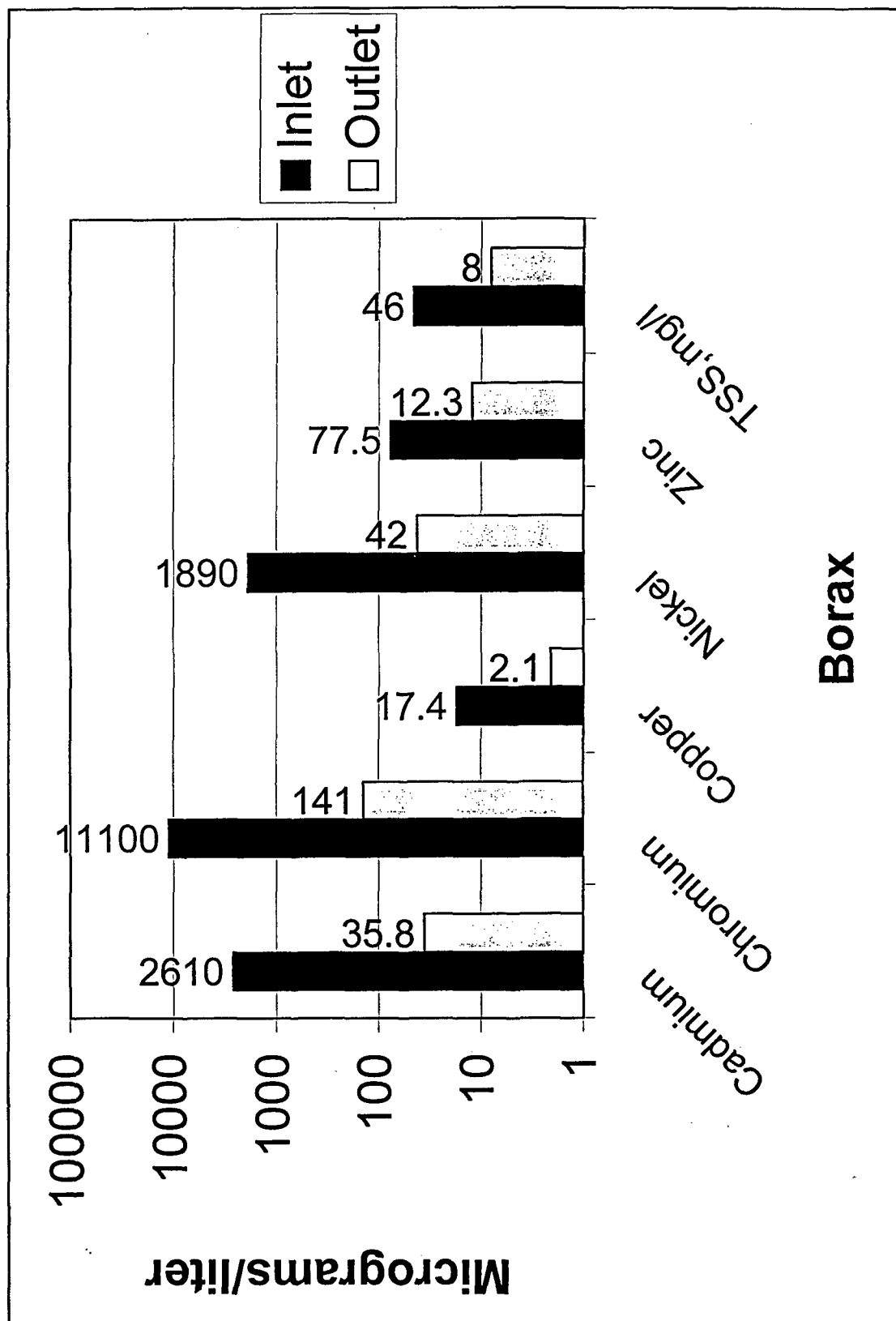


Figure 34. Borax Addition Test Metals Concentration.

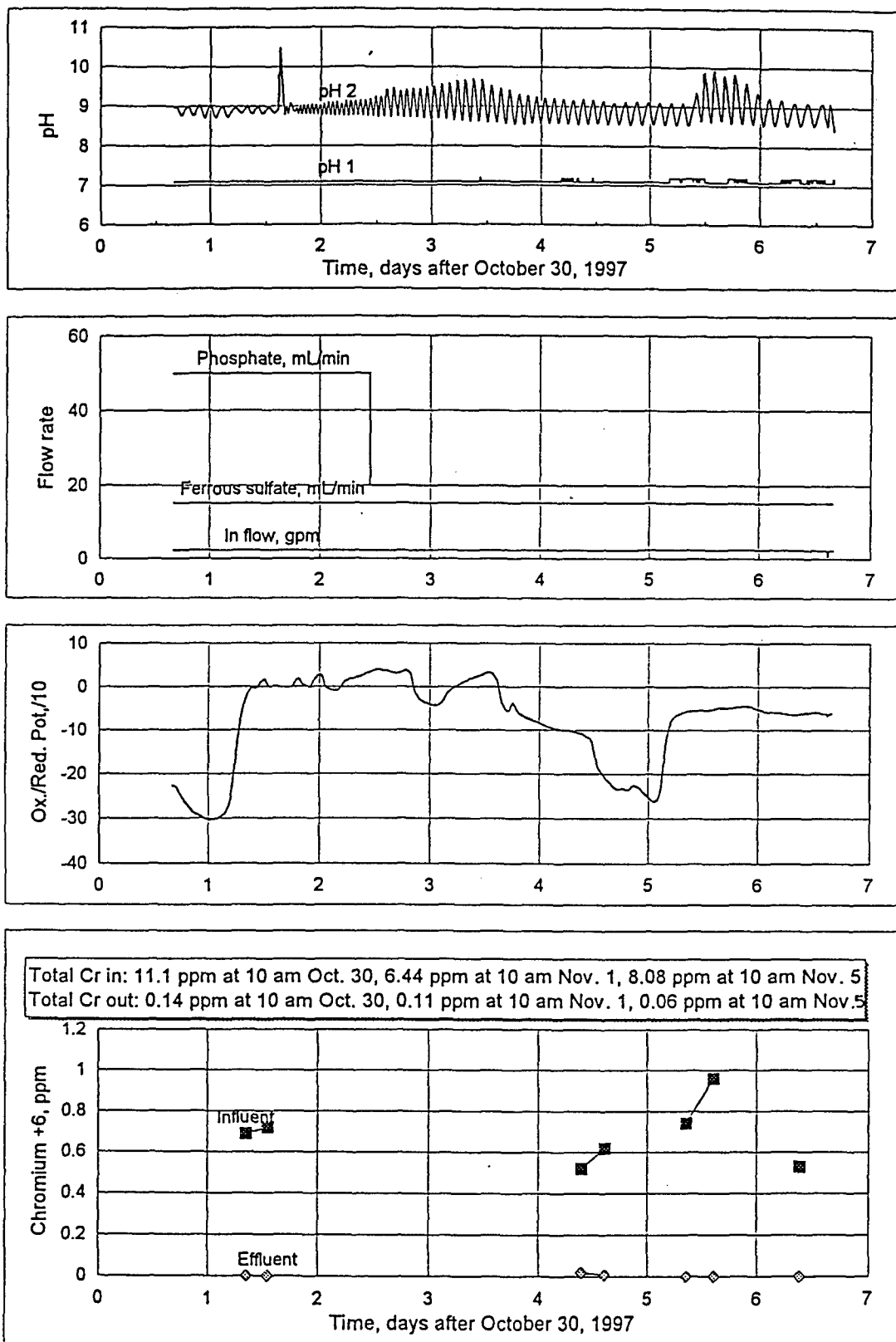


Figure 35. Phosphate Addition Test Operational and Analytical Data.

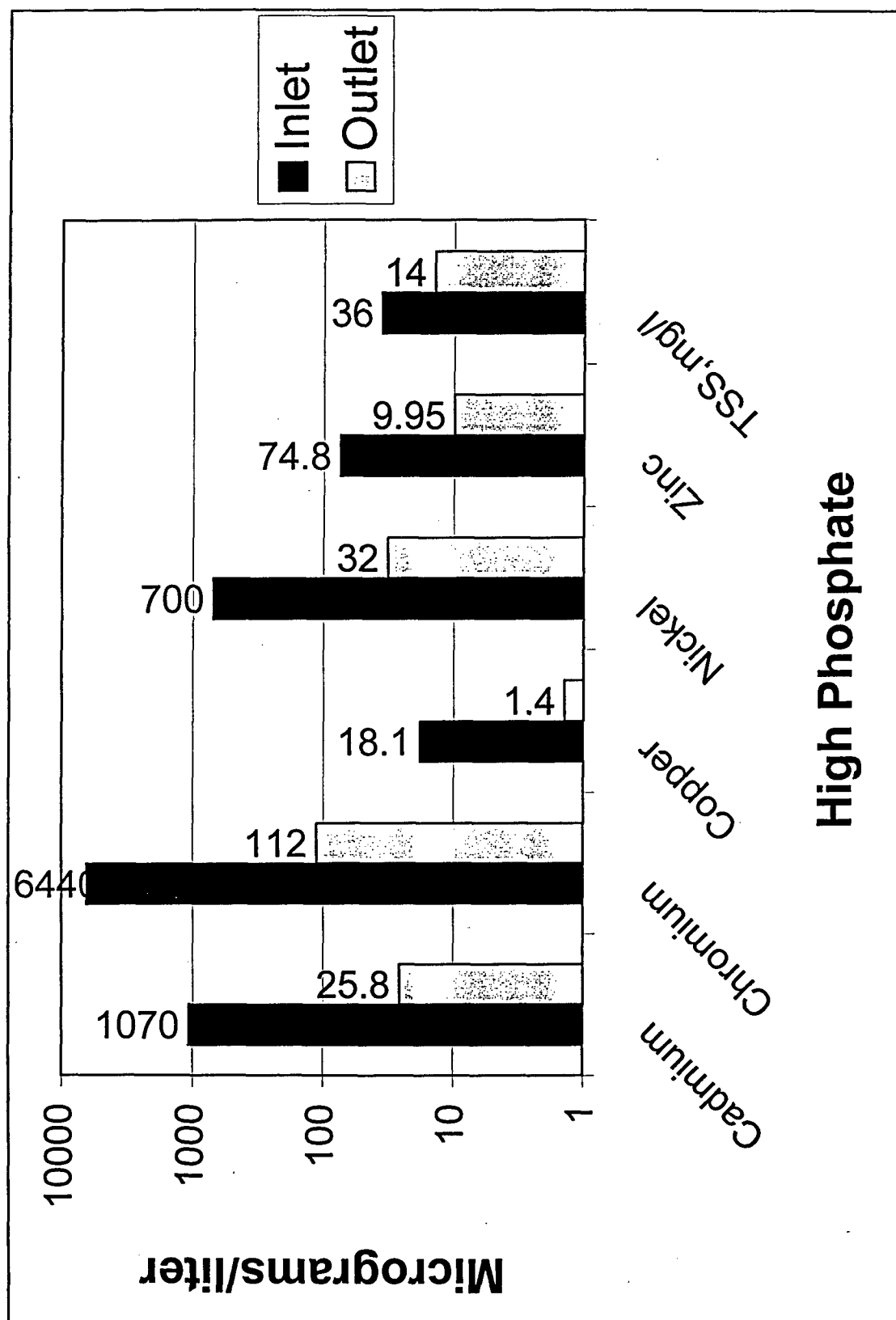


Figure 36. Metals Concentrations at High Phosphate Addition Rate.

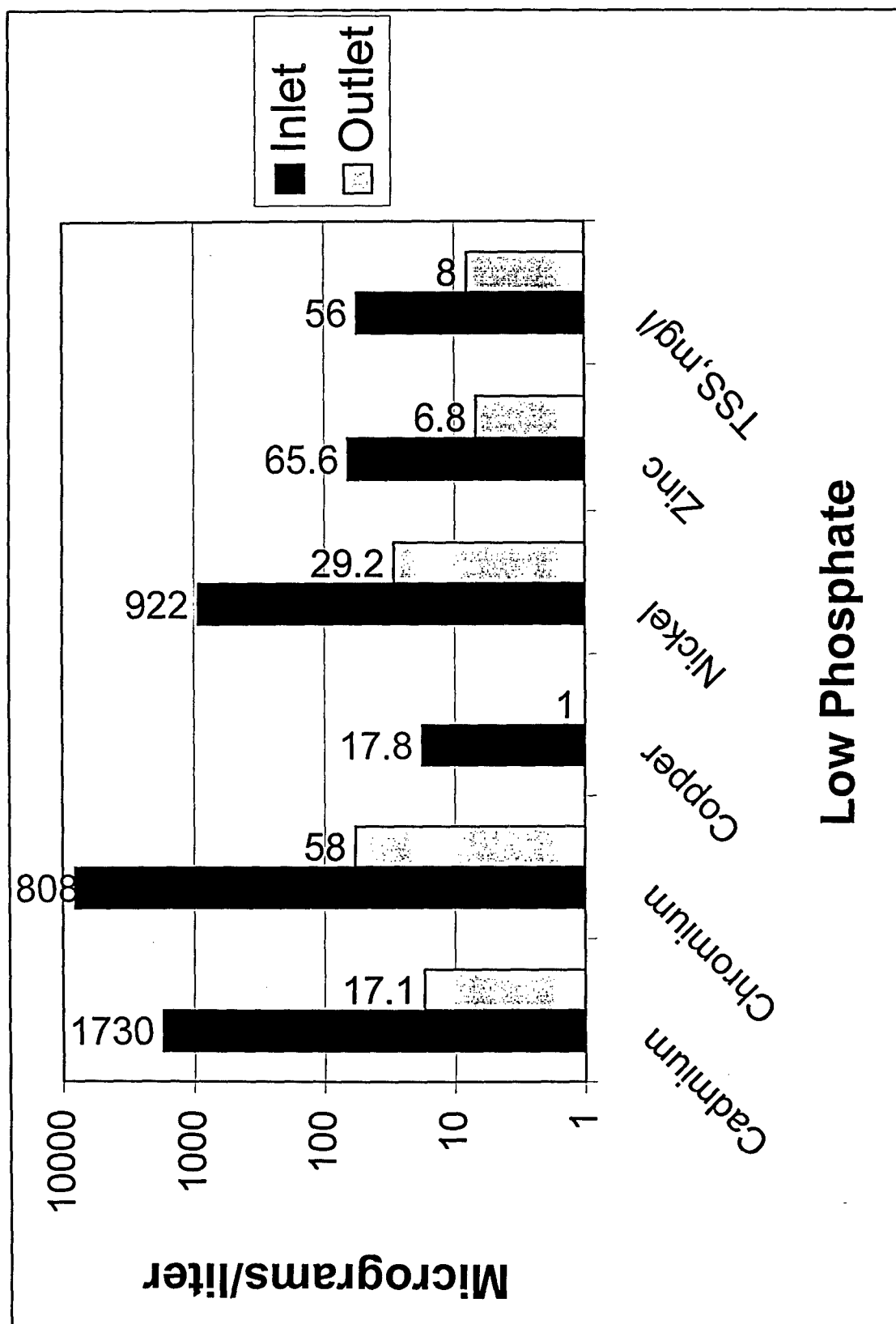


Figure 37. Metals Concentrations at Low Phosphate Addition Rate.

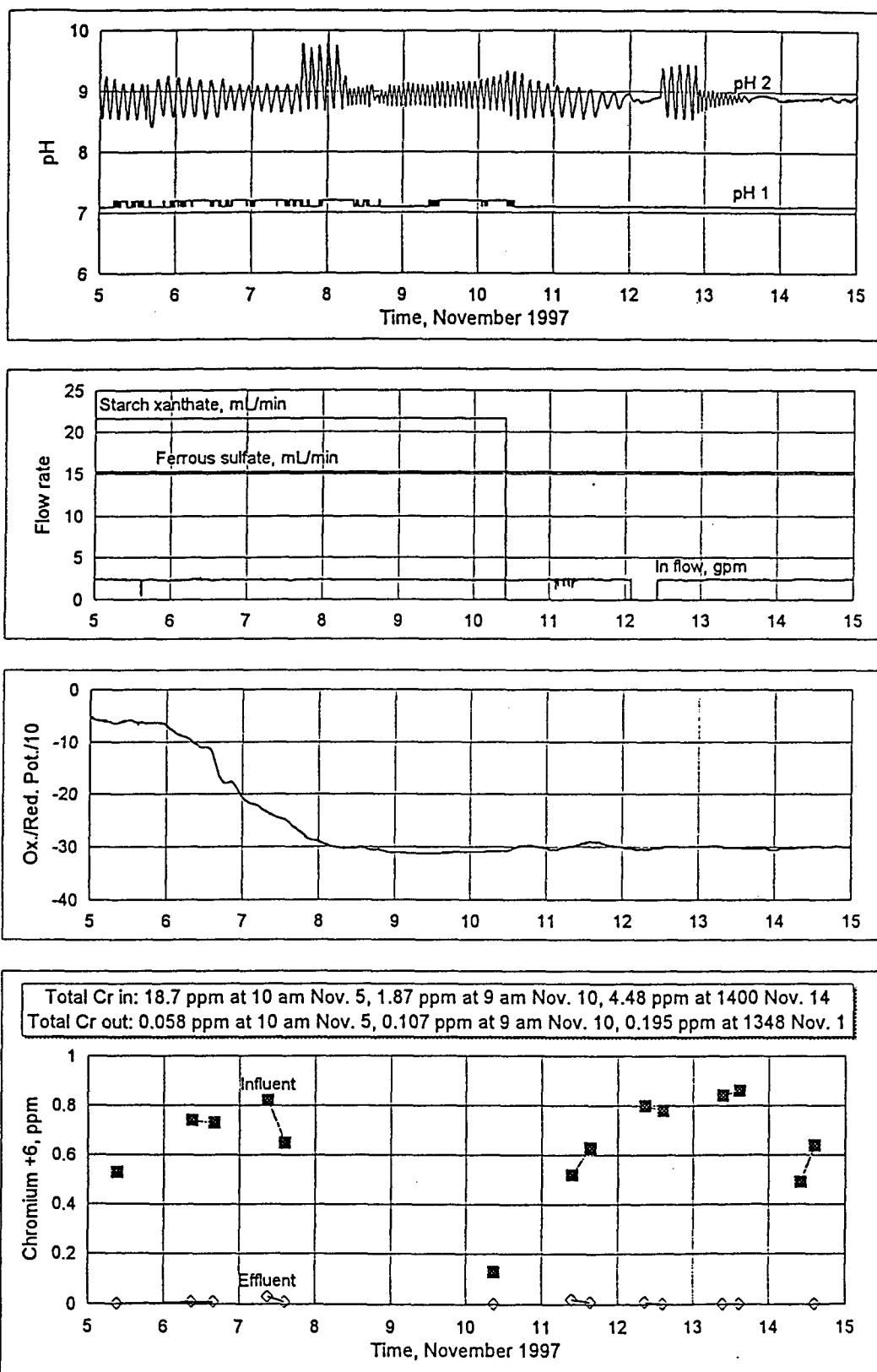


Figure 38. ISX Addition Test Operational and Analytical Data.

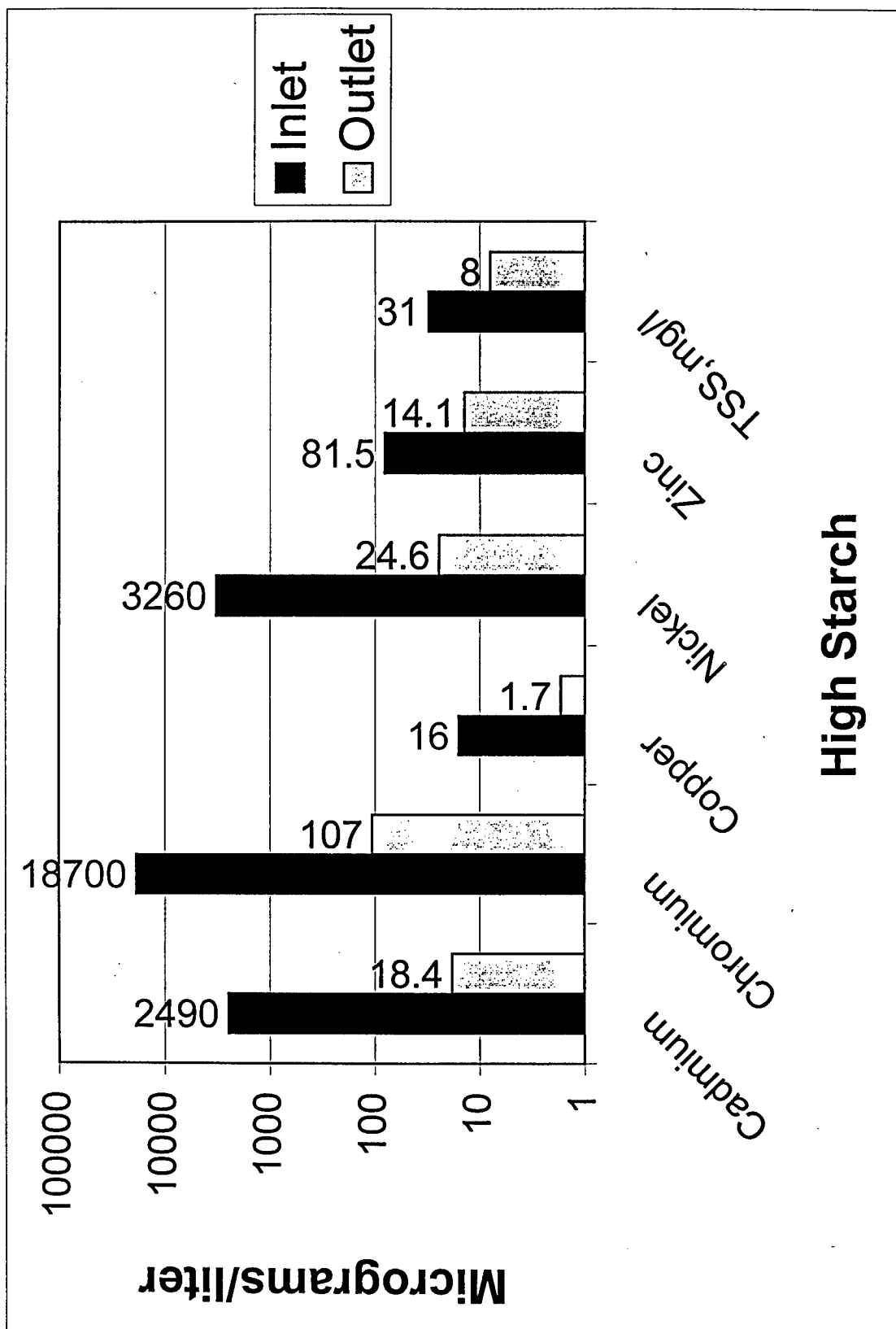


Figure 39. Metals Concentrations at High ISX Addition Rate.

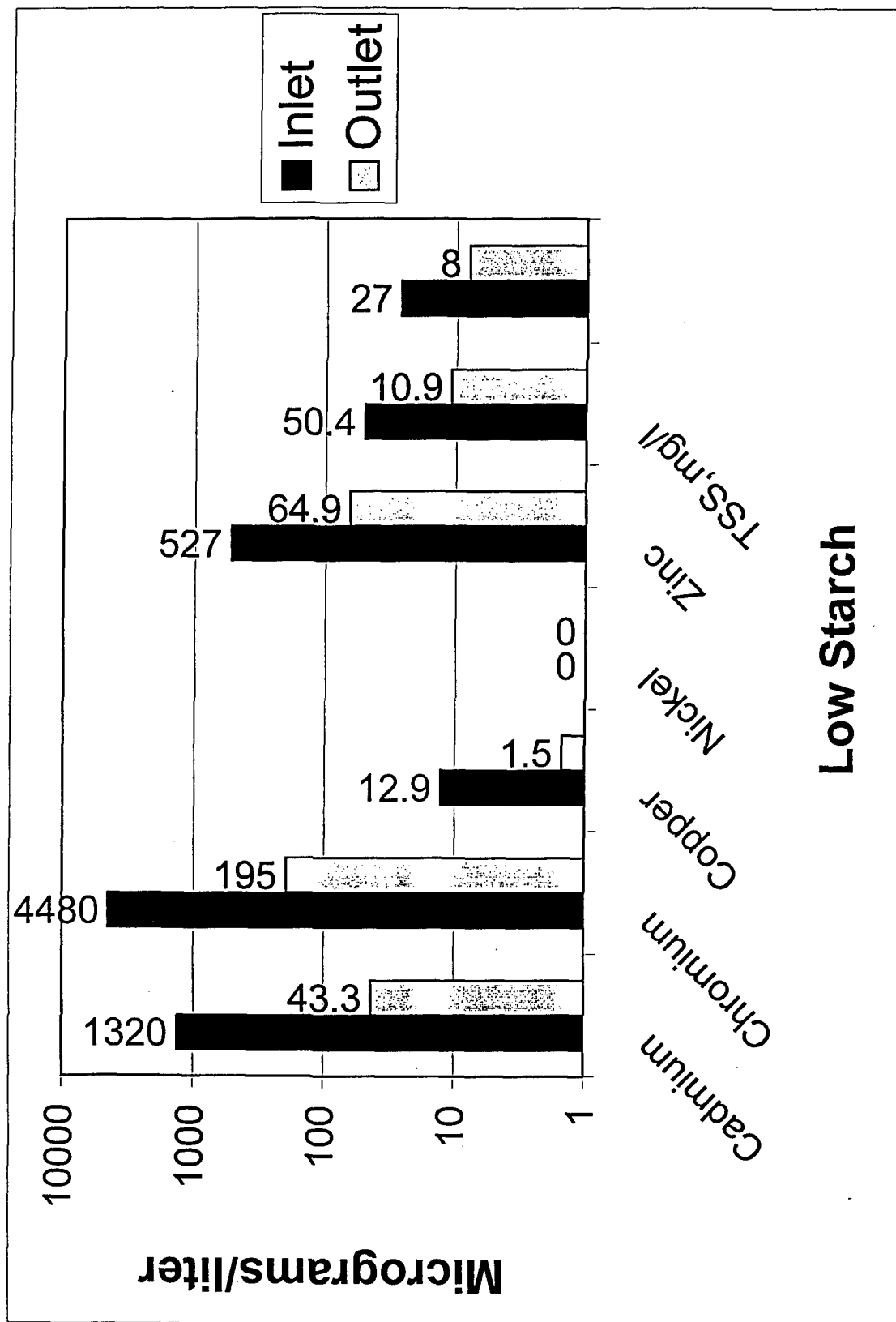


Figure 40. Metals Concentrations at Low ISX Addition Rate.

13. Reproduction of Minimum Ferrous Sulfate, Effect of Recycle Blanket

Attempts were made to reproduce the minimum ferrous sulfate test conditions. The ferrous sulfate feed was reduced from 15 mL/min to 10 mL/min. Since the sludge recycle made mix tank 3 contents appear black, hexavalent chromium samples were taken from mix tank 2. At 10 mL/min of ferrous sulfate addition, hexavalent chromium was still present, so the feed rate was increased to 20 mL/min. Hexavalent chromium was still present at this increased addition rate. The feed rate was increased again, this time to 57 mL/min. Hexavalent chromium was still present at mix tank 2, but not at the outlet of the SCC. Samples were taken from mix tank 3 and allowed to settle for less than 5 minutes. The supernatant was taken and analyzed for hexavalent chromium; none was found. It appears that the residual iron in the sludge is sufficient to reduce the hexavalent chromium. This result is also consistent with a slow hexavalent chromium reduction rate by colloidal or particulate ferrous hydroxide at pH >6.5.

The ferrous sulfate rate was continued and the sludge recycle was stopped to return the pilot plant to the operating conditions that were used for the first ferrous sulfate addition runs. At these conditions, the influent hexavalent chromium concentration was 0.76 mg/L, the mix tank 3 concentration was 0.55 mg/L, and the concentration in the effluent from the SCC was 0.31 mg/L. The ferrous feed was then stopped and the sludge recycle restarted. After 10 minutes, the hexavalent chromium level in mix tank 3 had returned to zero. This result confirms the above conclusions. The sludge recycle rate was 600 mL of sludge every 100 seconds. The sludge analysis gave the solids content of the sludge at 6.5 percent solids. The solids contained 6180-mg iron per kilogram solids. Based on this analysis and the recycle rate, the iron content of mix tank 3 was 4.2 mg/L. This is total iron, the amount of ferrous was not analyzed.

The ferrous iron content of the ferrous sulfate feed tank was checked to confirm that there was indeed ferrous iron. A Baker test strip was used; this strip contains a chemical pad that changes color based on the ferrous ion concentration. The test strip indicated over 100 mg/L in the feed solution (the maximum color on the strip). The solution was then diluted 1000 to 1, the test strip indicated about 5 mg/L, which would indicate about 5000 mg/L in the feed solution. The ferrous ion disappeared quickly in the dilute solution, within seconds no ferrous was seen in the 1000-to-1 dilution.

14. General Results

The turbidity of the influent and effluent from the pilot plant was measured daily. When samples for metals analysis were taken, the total suspended solids (TSS) were determined. Plotting the influent and effluent turbidity verses the TSS results in the plot shown in Figure 41. The influent data do not suggest a good correlation between the two. In contrast, the effluent data do suggest that a reasonable correlation exists. The use of a linear relationship allows one to estimate the effluent TSS based on the turbidity of the sample. For example a turbidity of 100 would correlate to a TSS value of 53 mg/L in the data in Figure 41.

This allows the turbidity of the effluent to be used to estimate the TSS of the effluent. Since the influent data does not correlate, an average value of 55 mg/L was used. The past data support this, the average TSS for the week of July 21, 1997 was 51 and the average for the pilot plant testing was 60.6. By using an average influent TSS and the estimated TSS based on the effluent turbidity, the difference plus the metal sulfides and hydroxides formed provides an estimate of the solids removed by the pilot plant process. Several samples were taken during the test for the TSS leaving mixing tank 3. The TSS analysis showed 100 to 150 mg/L during the reduced ferrous test and 120 to 130 mg/L during the minimum ferrous test. The metals (iron from ferrous sulfate, cadmium, nickel, and chromium from spike) contribute 26 mg/L during the reduced ferrous test and 18 mg/L during the minimum ferrous test. The polymers, which were added to form flocs, added 0.5 mg/L to the TSS, assuming that all of the polymer was attached to the solids. Using the above information, much more TSS was leaving mixing tank 3 than what can be accounted for based on the TSS in and what was added. Also based on the pilot plant TSS to the SCC and the actual plant TSS going to the SCC, the pilot plant is producing sludge at twice the rate of the actual plant. The actual IWTP at Tinker plant uses a chemical process that has been shown in past work (ref 1) to minimize sludge formation. The iron sulfate used in the pilot plant is known to act as a coagulant, which would increase solids formation. This may increase sludge formations but will produce cleaner effluents. The key is to use the above results to minimize the ferrous sulfate used.

The sludge amount the pilot plant produced during operation was small. The original plan was to waste sludge at a constant rate to maintain a stable sludge blanket in the SCC. However, during operation it was found that to maintain a good sludge blanket in the

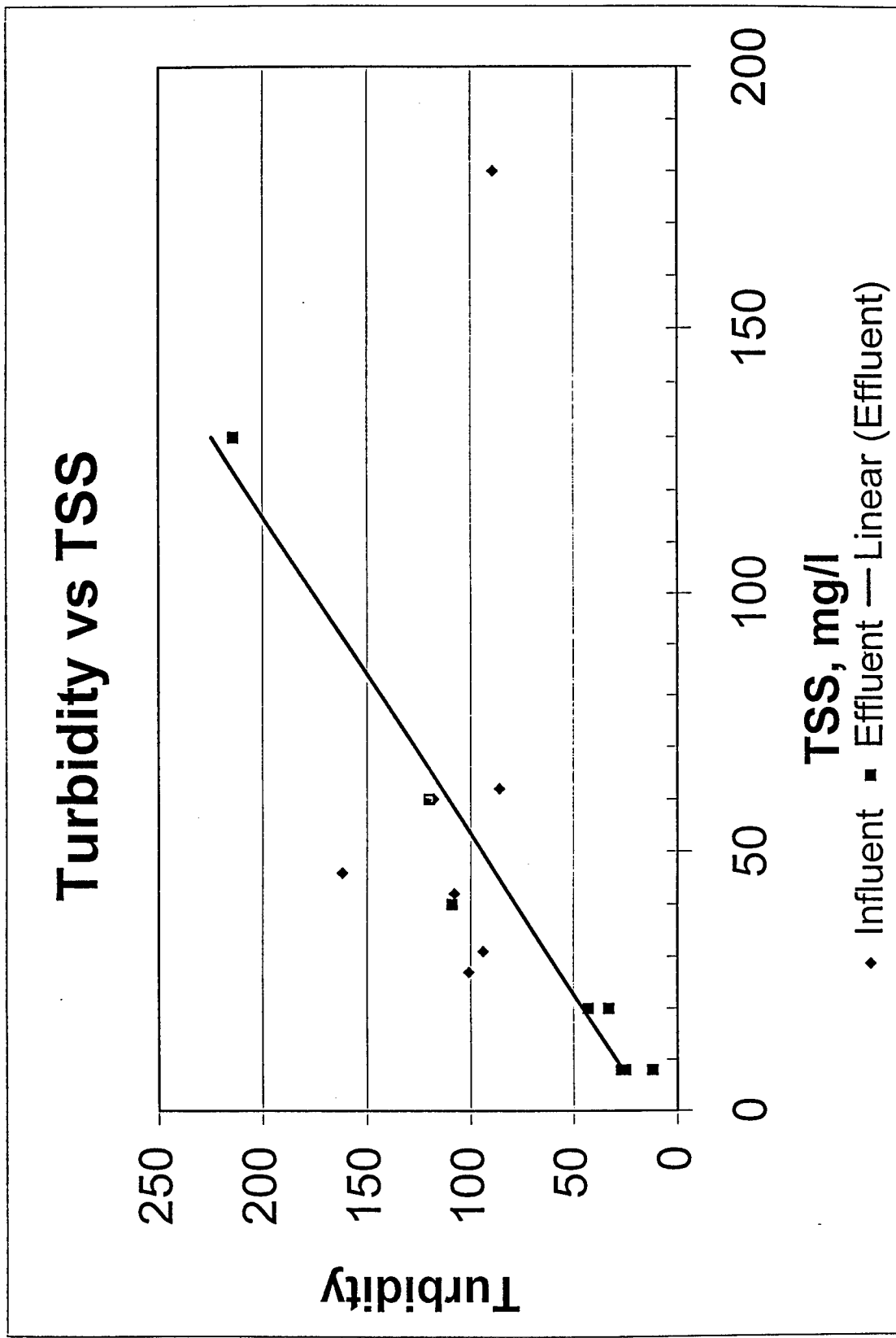


Figure 41. Turbidity Versus TSS.

SCC, none could be wasted. Near the end of pilot plant operation, several samples of the sludge were taken to determine both the solids content of the sludge in the bottom of the SCC and the iron content of this sludge. The sludge solids content ranged from 5.1 to 6.8 percent solids. Since the sludge was initially created by the use of high amounts of ferrous sulfate, it was expected that the iron content of the sludge would be high, over 10 percent. The iron analysis of the sludge showed an iron concentration of 5330 to 6180 mg/kg of dry solids (0.5 to 0.6 weight percent). This also supports the results that show large amounts of non-iron sludge originated from the influent. These solids have to be formed in the process since they are not entering the pilot plant as solids, for example silicates, aluminum hydroxide, magnesium hydroxide, carbonates, etc. All of these materials would be expected to precipitate with pH adjustment from 4-7 to 8-10.

D. RESULTS AND CONCLUSIONS

After the sludge blanket started to form, the recycle point was switched from the 2-foot level to the SCC bottom to allow for sludge recycle. During the sludge blanket build up it was observed that the higher the sludge recycle rate the higher the effluent water turbidity from the SCC. The lowest effluent turbidity was achieved while the SCC was operated as only a clarifier with no sludge recycle.

It was noted that the SCC did not have the degree of mixing in the center well, as does the full-scale SCC. To increase the mixing of the recycled sludge to correlate better with the full-scale SCC, the sludge recycle that was going to the static mixer was moved to mix tank 3. This provided more extensive mixing of the recycled sludge with the newly formed flocs. This improved the effluent water turbidity. The amount of sludge recycle was 600 mL every 100 seconds into mix tank 3. The solids content of the recycled sludge was found to range from 5 to 6 percent solids.

After the sludge blanket was formed by feeding excess ferrous sulfate, the ferrous sulfate feed rate was set to produce a baseline concentration of 21 mg/L in mix tank 1. Cadmium, chromium, and nickel were all reduced by more than 90 percent, while copper and zinc were reduced by about 80 percent. The copper and zinc were not removed as extensively, on a percentage basis, as the other metals due to their low concentrations in the influent waste water.

Reducing the ferrous sulfate feed rate to mix tank 1 to an amount giving about half the baseline concentration in mix tank 1, or 10 mg/L, did not decrease removal efficiency. No hexavalent chromium was detected in the SCC effluent. Other metals removals at the reduced ferrous sulfate operating conditions were comparable to the baseline condition.

To determine the minimum ferrous sulfate feed rate needed to completely reduce the hexavalent chromium, the ferrous sulfate feed rate was reduced until hexavalent chromium was detected at mix tank 3 and then increased slightly until the hexavalent chromium concentration returned to zero. The minimum ferrous sulfate feed rate was the amount that gave an 8 mg/L concentration in mix tank 1. Other metals removals were better for the 10 mg/L test, but their influent concentrations were also decreased.

Borax was added to mix tank 2 to evaluate whether the buffer would improve the ability to control process pH and, in turn, improve metal removal efficiencies. Based on the percent metals reduction, borax addition did not significantly enhance metals removal. pH control was smoothest when the dilute sodium hydroxide solution was used for control. Better pH controller tuning with the use of dilute sodium hydroxide would be less expensive than using borax as a buffer.

Sodium phosphate addition was tested to determine whether additional trivalent chromium removal could be achieved with this additive. The lowest effluent concentrations of total chromium, at 58 $\mu\text{g/L}$, were achieved with the use of sodium phosphate. Total chromium concentrations increased after the phosphate addition was stopped.

Starch xanthate was tested as a polishing agent to improve divalent metals removal by the SCC blanket. The lowest effluent concentrations of nickel were achieved using the starch, as were the highest removal percentages for cadmium and nickel. Removal efficiencies increased as starch addition rate was increased. Subsequent reduction of the starch feed rate resulted in corresponding decreases in cadmium and nickel removal.

The overall conclusion of the pilot plant testing was that better metals removal by the SCC blanket could be achieved with the use of polishing compounds such as starch xanthate and sodium phosphate. The use of borax for pH control does not appear to offer benefits commensurate with its increased cost.

Based on test results, it is recommended that the adoption of the SCC blanket technology be considered for more widespread Air Force use. Ferrous sulfate use can be reduced, thereby

decreasing waste quantities generated. Use of sodium phosphate for increasing total Cr removal and ISX for increasing Cd and Ni removal can be decided on a case-by-case basis.

E. REFERENCE

1. Wikoff, P. M., Suciu, D. F., Prescott, D. S., et al., "Full-Scale Implementation of the Sodium Sulfide/Ferrous Sulfate Treatment Process — Phase III," AFESC Engineering & Services Laboratory, Air Force Engineering & Services Center, Tyndall Air Force Base, Florida, February 1989.

SECTION V

LOW TEMPERATURE SLUDGE DRYING

A. INTRODUCTION

Disposal costs for the sludge produced at IWTPs are proportional to the mass or volume of disposed sludge. Therefore, removing excess water from contaminated sludge has been identified as a cost-effective treatment process. Mechanical dewatering methods such as pressing and centrifugation are typically used to lower sludge moisture content to levels near 35 to 40 percent solids. Mechanical methods alone, however, generally cannot meet a target disposal moisture content of 70 percent solids. Findings from Phase I of this project suggested that mechanical methods in conjunction with thermal drying technologies can meet or exceed the 70 percent solids criteria.

Thermal drying technologies are often used for dewatering applications, but these can have several drawbacks. The process can generate cross-media pollutant streams and often requires the heating of large air volumes, resulting in high operating costs. Based on findings from Phase I of this project, a cost-effective dryer technology designed to minimize the potential for cross-media pollution was recently purchased and installed at the OO-ALC. The dryer technology, a JWI J-Mate Low-temperature Dryer, uses a closed loop system to minimize both energy demands and pollutant emissions to the atmosphere.

A diagram illustrating the JWI low-temperature drying process is provided in Figure 42. The JWI dryer uses a closed loop air system to remove moisture from batches of IWTP sludge following filter press operations. IWTP sludge, initially containing 35 to 40 percent solids, is introduced to the system by placing it in carts that connect to the dryer ducting loop. Moisture is entrained by passing warm air up through the louvered cart bottoms through the sludge. The process air is then routed to a dehumidifier where moisture is condensed out of the air stream onto cooling coils. The air passes through the blower into the air heating section where heat generated by the refrigeration warms the air prior to beginning the cycle again.

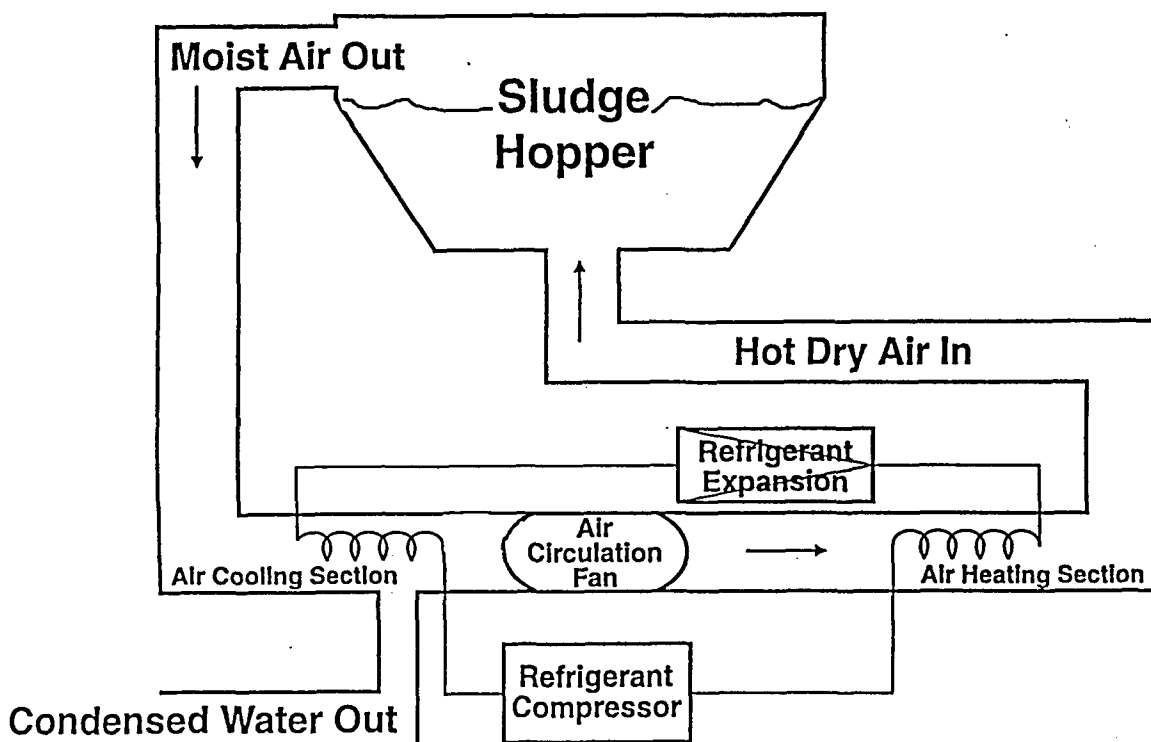


Figure 42. JWI J-Mate Low-Temperature Dryer.

B. OBJECTIVE

The field test objective was to evaluate the JWI dryer system based on the following criteria:

- Sludge drying effectiveness
- Potential for cross-media pollution
- Economic assessment

C. TEST PLAN

A series of field tests were performed on the JWI J-Mate Low-Temperature Dryer technology installed to treat IWTP sludge at the OO-ALC and Lawrence Berkeley National Laboratories (LBNL) facilities. This section summarizes the test parameters and procedures that were employed to accomplish the dryer evaluation testing.

1. Experimental Apparatus — OO-ALC

The dryer performance evaluation at OO-ALC was performed on a JWI-210 closed loop drying unit. Under normal operating conditions, a dryer cycle runs for 12 to 14 hours depending on sludge consistency off the filter press. The dried sludge is fork-lifted into large covered waste bins, located just outside of the building which houses the dryer units. OO-ALC runs 3 to 4 dryer cycles per week. The JWI sludge dryers were installed at the OO-ALC at the end of 1996. OO-ALC IWTP personnel were pleased with the dryer's performance and ease of operation. The sludge dryers treat industrial sludge from various operations on base. The JWI dryer units are housed in Building 577, located in the IWTP. The dryer sludge carts handle a volume of 37 cubic feet of sludge. The dryer is powered by electricity only, and operates on 208-230 volt, 47 amp circuit (design max). The dryer's power requirements consist of a refrigerator/heater unit and blowers for air. A 1½-inch PVC drain discharges condensate to a removable grate at ground level.

2. Experimental Apparatus — LBNL

The dryer performance evaluation at LBNL was performed on a JWI J-203 closed loop drying unit. Under normal operating conditions, a dryer cycle runs for 12 to 14 hours including loading, drying, and unloading, depending on sludge consistency off the filter press. The dryer sludge cake is drummed as waste and landfilled. LBNL runs 3 to 4 dryer cycles per week. The JWI sludge dryer was installed at LBNL in 1997. During the pre-test interview, LBNL operators were pleased with the dryer's performance, noting that it worked well in reducing sludge volume by half. The operators also noted the dryer was easy to install and operate. The sludge dryer treats metal hydroxide sludge from plating operations. The JWI dryer unit is located outside of the plating facility, in a covered pad area. The sludge cart for the dryer handles a volume of 11 cubic feet of sludge. The dryer is powered by electricity only, and operates on a 220 volt, 17 amp circuit (design max). The dryer's power requirements consist of a refrigerator/heater unit and blowers for air. A 1½-inch PVC drain discharges condensate to a removable grate at ground level.

3. Experimental Procedure

The dryer performance evaluation strategy was developed to measure critical parameters during normal dryer operation. Characteristics of both the sludge and dryer were monitored during each test cycle. This section outlines the specific tests that were performed, and describes the methods that were used to measure each test parameter. Two test events were performed at each location to evaluate the performance of the JWI J-Mate Low-Temperature Dryers. Table 16 summarizes the measurement parameters and lists the method, sample duration, sample frequency, and the number and type of QC samples that were collected. These parameters were monitored for the two drying cycles in order to evaluate dryer effectiveness, potential for cross-media pollution, and economics of the system.

4. Sludge Drying Effectiveness

Dryer effectiveness was assessed by quantifying the dryer's ability to remove moisture from the sludge within a reasonable time. The total mass of each sludge batch was measured gravimetrically before and after each drying cycle to determine the mass of moisture removed. The pre- and post-test weights of the cart containing sludge was measured using a platform scale. An empty sludge cart tare weight was measured and the sludge mass was determined by subtracting the tare weight from sludge and cart combined measurement.

Because vehicle scales do not provide the sensitivity necessary for the purpose of this test program, sludge grab samples were also collected directly before and following each drying cycle for density analysis. A representative sludge sample was collected for mass determination, moisture, and VOC analyses. A homogeneous grab sample for each analysis was collected after mixing the sludge with a shovel. Sludge density was determined gravimetrically by collecting a known volume of sludge and measuring the sample weight before and after excess moisture is removed using direct heat. Sludge moisture content was measured using a balance in general accordance with ASTM Method D4959 and EPA Method 160.3 (Total Solids). Sludge density measurements were coupled with volume measurements to determine sludge mass.

TABLE 16. SLUDGE DRYER TEST MATRIX.

Parameter	Measurement Equipment/ Collection Media	Method/ Principle	No. Samples per Run	Sample Duration	Sample Frequency	QC Samples
Mass of sludge	vehicle scales	Gravimetric	2	NA ^a	Pre and Post	1 duplicate ^b
	2 x 250 ml glass jars	Volumetric/ Gravimetric	8 (4 pre, 4 post)	NA	Pre and Post	1 duplicate
Volume and appearance of sludge	tape measure	Visual observation	2	NA	Pre and Post	NA
Sludge moisture content	2 x 250 ml glass jars	ASTM D4959	2	NA	Pre and Post	1 duplicate
Condensate removal rate	graduated cylinder	Volumetric	Various	60 seconds	30 minutes first 2 hours, hourly thereafter based on personnel availability	1 duplicate per run
Temperatures of sludge, air entering and exiting cart	Type-K thermocouples	NA	Continuous	5 minutes	continuous	calibrated system
Speciated VOC in condensate	40 mL VOA vials	EPA SW-846 Method 8260	3	NA	Proximate to test beginning, middle, and end	1 duplicate ^b , 1 blank
Speciated VOC in sludge	125 mL glass jars	EPA SW-846 Method 8260	2	NA	Pre and post	1 duplicate ^b , 1 blank
Flowrate of air leakage	Hot wire anemometer	ACGIH	2	NA	Proximate to test beginning and end	1 duplicate ^b
Speciated VOC in air loop	SUMMA ^c passivated canister	EPA TO-14	2 (inlet, outlet)	6 hours	Mid-cycle	1 duplicate ^b , 1 blank
Dryer electricity usage	Ammeter	NA	2	NA	Proximate to test beginning and end	NA

^a NA = Not applicable.

^b One duplicate performed for the entire test event

^c Air flow through any gaps in the system with leakage is measured

In addition, visual observations were made in conjunction with moisture measurements to verify sludge moisture content uniformity. Before and after each test run, the volume of sludge was determined using a tape by measuring the sludge depth in the cart, as well as the length and width of the cart. The visual appearance of each sludge batch was also noted and recorded on the field data sheet before and after each run.

The sludge moisture removal rate was quantified by periodically measuring the rate at which condensate was draining from the system. The condensation accumulation rate was measured volumetrically at 30 minute intervals for the first 2 hours of operation, and at 10 to 30 minute intervals thereafter, based on personnel availability. A normal drying cycle ends when the sludge reaches 10 percent moisture or the drying rate drops below one percent per hour based on the initial moisture level. A nominal drying time of 12 hours was established as part of this test program. Condensation removal rate information was used to assess drying completeness and provide the data necessary for developing a batch drying curve for the system.

Temperature data trends provide information related to dryer performance during the cycle. Temperatures of the sludge, air entering the sludge, and the air exiting the sludge were monitored and recorded throughout each dryer test using type-K thermocouples. Thermocouples were placed at three depths in the sludge, and in the heating and cooling ducts of the JWI dryer system. Temperature was monitored continuously at each location, and averaged and recorded at 1 minute intervals using a data-logging system. The temperature measurement system was calibrated prior to the test events according to EPA procedures, to ensure accurate temperatures were measured and recorded within the dryer.

5. Potential for Cross-Media Pollution

Because the drying processes can result in cross-media contamination, the potential for volatile organic compound (VOC) emissions to the environment through air and water process streams were evaluated. Grab samples of dryer condensate were collected at the beginning, middle, and end of each drying cycle for speciated VOC analysis. Condensate samples were collected per the procedure identified in EPA SW-846, Ch. 4, Sec. 4.1. Condensate was collected in 40 mL glass VOA vials with Teflon-lined silicone septa. The effluent was gently poured into the vial to avoid bubbling and minimize loss to volatile compounds. Vials were completely filled to eliminate headspace. All samples were stored at

4°C prior to analysis. One duplicate and one blank sample were collected and analyzed to assess measurement precision and background contamination levels, respectively.

The condensate samples were analyzed for VOC concentrations following SW-846 Method 8260. Concentrations of speciated compounds were quantified by gas chromatography/mass spectrometry (GC/MS). The VOCs were introduced into the GC using a purge and trap method. Following compound separation in the GC, analytes are detected by the MS. The analysis was conducted by Sequoia Analytical Laboratory in Redwood City, California.

In order to identify speciated VOC concentrations in the sludge, sludge samples were collected per the procedure identified in EPA SW-846, Ch. 4, Sec. 4.1. The samples were collected prior to and following the sludge drying cycle. Sludge was collected in 125 mL glass amber bottles with Teflon-lined caps. The samples were stored at 4°C prior to analysis. The sludge samples were analyzed for VOC concentrations following SW-846 Method 8260. Sequoia Analytical Laboratory performed the analysis.

The JWI dryer uses a closed loop system and, under normal operation, should possess negligible air emissions. However, minor air escape routes were identified for the dryer at OO-ALC, and the flowrate was estimated using a hot-wire anemometer. The flowrate exiting the system from gaps between the sludge dryer and the cart was determined following the ACGIH method for determining open face flowrates using a hot wire anemometer.

VOC concentrations in the dryer air stream were measured at the inlet and outlet during each drying cycle. Air samples within the dryer air loop were collected and analyzed following EPA Method TO-14. Sample gas was drawn into an evacuated SUMMA® canister through a critical orifice that maintains a predetermined constant flowrate. The canister valve is closed after sampling is complete. Speciated VOC concentration levels in the sample gas were determined following GC/MS procedures. The gas analysis was performed by Air Toxics, Ltd. in Folsom, California. One duplicate and one blank sample were collected and analyzed to assess measurement precision and background contamination levels, respectively.

Background VOC concentration levels were also determined for the dryer at OO-ALC. One sample was collected in close proximity of the dryer, to access leaks in the dryer loop. Another sample was collected near the center of Building 577 to access background VOC

concentration levels in the building. The dryer unit at LBNL is located outside, therefore, background VOC concentrations were not measured.

6. Economic Assessment

Operating costs of the JWI system were assessed by quantifying power consumption and labor demands necessary to operate the dryer. Actual electric power usage was estimated by measuring the total system amperage (amp) using a clamp-on ammeter. These measurements were compared with the motor ratings of the compressor and blower. As part of the electric power usage monitoring, differential pressure (ΔP) measurements were also recorded in the filed notebook. Labor requirements were estimated by conducting interviews with facility employees assigned to operate the system.

Given dryer electricity usage rate and operating labor requirements, the operating cost was estimated using the following expression:

$$\text{Operating Cost (dollars)} = (V \cdot A \cdot 10^{-3} \cdot \text{BDT} \cdot \text{UC}) + (\text{LR} \cdot \text{PR}) \quad (3)$$

where: V = voltage measurement (volts)

A = ammeter measurement (amps)

BDT = batch drying time (hrs)

UC = local utility energy cost (dollars/kw-hr)

LR = system labor requirements (hrs/batch event)

PR = loaded pay rate of operating personnel (dollars/hr)

D. RESULTS AND DISCUSSION

1. Sludge Drying Effectiveness

The mass of sludge (pre and post), sludge moisture content (pre and post) and condensate removal rate measurements were taken to determine sludge drying effectiveness of the JWI J-Mate dryers. Where applicable, the measurement method precision was assessed via replicate measurements. Accuracy of these measurements was determined by calculating the total moisture loss per run from each of the three measurements and comparing the results.

a. Results for OO-ALC. The original test matrix at OO-ALC called for testing four complete drying cycles. Test personnel were only able to complete two of the four tests before the dryer units were shut down due to problems with the IWTP. The two tests that were completed represent worst case scenarios of drying poorly dewatered cake release from the filter press. The sludge sampled in these two drying cycles was too wet with a solids content of approximately 21 percent solids. Typically, sludge coming off a filter press in an IWTP, such as the OO-ALC's, should have a solids content of 35 to 40 percent solids. The tests were performed with the same batch of sludge released from the filter press. Test #1 was started about an hour after the sludge was released from the filter press into the two sludge carts. Test #2 was performed with the second sludge cart approximately 14 hours after the sludge was released from the filter press.

As part of the test matrix to evaluate the dryer's effectiveness, the total mass of each sludge batch was to be measured gravimetrically before and after each drying cycle. To perform these weighings, test personnel secured the use of an OO-ALC vehicle scale. However, the vehicle scale was not in working order during the week of testing. Test personnel scrambled to rent a scale from a local vendor in Ogden, Utah. However, prior to the delivery of this unit the test program was halted as a result of problems with the IWTP. This was considered a crucial piece of data that test personnel were unable to collect.

Several grab samples were collected before and after each drying cycle to determine the density of sludge. Densities were determined by taking a known volume of sludge and analyzing it gravimetrically. This data was used to assess the drying effectiveness of the dryers. Table 17 presents the results of these measurements.

The volume and appearance of the sludge was assessed prior to and following each drying cycle. The volume of the sludge was determined using a yardstick to measure the depth of the sludge in the cart. During the two drying cycles that were tested, an average volume reduction in the amount of the sludge was calculated at approximately 1.5 cubic feet. The volume measurements were approximated due to the difficulty in measuring the non-uniform sludge. The visual appearance of the sludge indicated drying on the corners and bottom, following drying cycles.

TABLE 17. SLUDGE PARAMETERS MEASURED TO DETERMINE DRYING EFFECTIVENESS, OO-ALC.

Test Date	Duration of Drying Cycle (hrs)	Pre Weight (grams)	Pre Density (g/ml)	Post Weight (grams)	Post Density (g/mL)	Weight Reduction (grams)	Percent Reduction
9-16-97	12	548.1	1.096	495.3	0.991	52.8	9.6
9-17-97	12	611.7	1.223	546.9	1.094	64.8	10.6
Average	12	579.9	1.160	521.1	1.043	58.8	10.1

The moisture content of the sludge was measured by OO-ALC, IWTP lab personnel with a moisture analyzer in general accordance with ASTM Method D4959. The results of the sludge samples analyzed for moisture content on Runs 1 and 2 were inconclusive. Pre and post analysis of the sludge samples on Runs 1 and 2 were all around 21 percent solids. This is well below the typical range of 35 to 40 percent solids. From the results of the moisture content analysis, it appears that the sludge cake released from the filter press was too wet, and that the IWTP was having difficulty processing its sludge through the filter press and dryers.

The condensate removal rate was measured to assess the dryer's ability to remove moisture from the sludge. Figure 43 shows the batch drying curves for the system. During Run #1, the total condensate removed from the sludge was measured at approximately 190 L with an average condensate removal rate of 264 ml/min. During Run #2, the total condensate removed from the sludge was measured at 162 L with an average condensate removal rate of 225 ml/min.

The temperatures of the sludge (upper, middle and lower sludge), the air entering the sludge (inlet), and the air exiting the sludge (outlet) were measured and recorded throughout each drying cycle to assess the dryer's performance. Temperature data indicates a slow climb in the sludge temperature during the drying cycle, as the sludge dried from the bottom upward. The temperature data coincides with the visual observations made following the drying cycles. The corners and bottom-half of the sludge in the cart was drying, while the top portion remained wet.

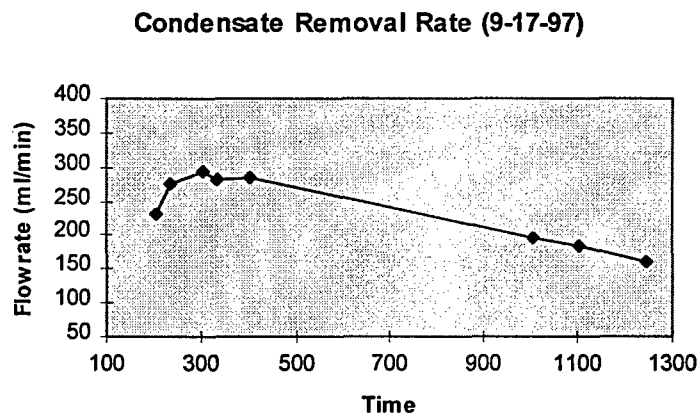
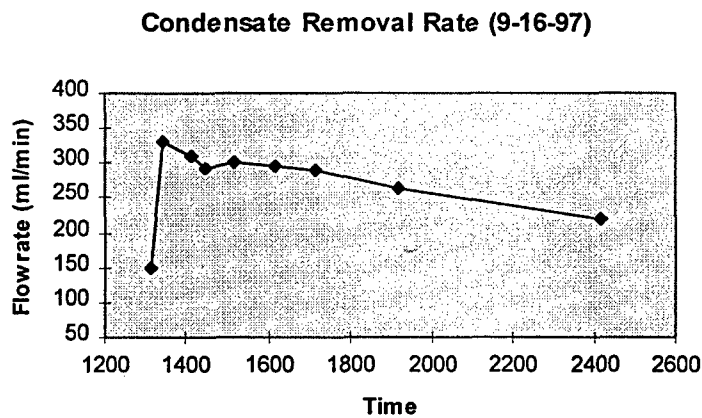


Figure 43. Sludge Dryer Condensate Removal, OO-ALC.

The lack of drying between the pre and post sludge samples is a result of the high moisture content of the initial sludge cake from the OO-ALC's IWTP press. The wet sludge clumps together in the cart and eliminates the porous surface area of the sludge required for thorough drying. It is the porosity of the compressed sludge cake that allows the warm air to move up through the sludge and dry it more evenly. However, it should be noted that the moisture content samples were collected near the center of the carts in the area of greatest hydrated solids.

b. Results for LBNL. One drying cycle was tested of the LBNL JWI J-203 dryer. As with the dryer tests at OO-ALC, the sludge cake released from the LBNL filter press contained a high moisture content of 87% moisture. The JWI dryer reduced the moisture content by only 8%. The poorly dewatered sludge cake resulted in the minimal evaporation and

inefficient drainability. Table 18 summarizes the sludge drying effectiveness results of the LBNL JWI J-203 dryer.

TABLE 18. DRYING EFFECTIVENESS SLUDGE PARAMETERS , LBNL.

	Total Batch Sludge Mass		Sample Sludge Mass ^a	Sludge Density	Sludge Volume		Moisture Content
	(lbs)	(kg)			(ft ³)	(m ³)	
Pre Drying	254	115	477.8	1.59	4.1	0.12	87
Post Drying	208	94	470.1	1.57	4.1	0.12	80
Difference	46	21	7.7	0.02	0	0	7
Reduction	18%	18%	1.6%	1.3%	0	0	8%

^a Sludge sample mass for 300 mL volume.

The sample sludge mass analyses shows only slight reduction in sludge weight after 12 hours of evaporative drying. The batch sludge mass analyses showed a slightly greater reduction in total batch weight, possibly a result of the non-homogeneous nature in moisture content of the sludge as it evaporates from the bottom. Based on visual observations, the sludge initial appearance was rust color and “pudding-like” in consistency. The sludge final appearance was similar in color and consistency, but appeared slightly dryer in the corners. There was no significant change in sludge volume following the drying process.

The condensate removal rate indicates the dryers ability to remove moisture from the sludge. For the LBNL test event, condensation removal rate information for the complete drying cycle was unavailable. Test personnel were required to leave the site before the drying cycle was completed. Therefore, condensate removal data was collected for only the first 4 hours of the drying cycle, and a complete batch drying curve for the system could not be developed. Condensate removal from the system began two hours into the drying cycle. For the initial 2.2 hours of the drying cycle, there was no condensate removal. For the next 2 hours, the average condensate removal rate was 13.5 ml/min. Figure 44 shows the condensate removal rate with time during a portion of the drying cycle.

LBNL Sludge Dryer Condensate Removal

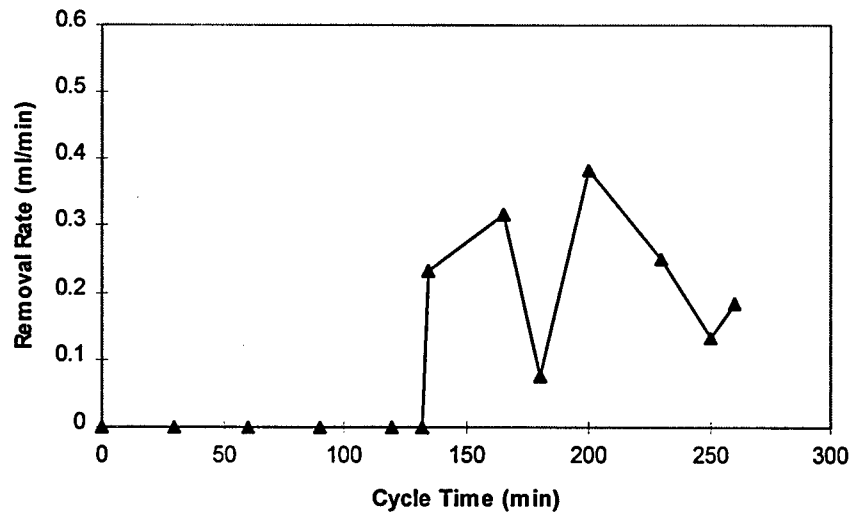


Figure 44. Sludge Dryer Condensate Removal, LBNL.

The LBNL JWI dryer performance was determined by correlating trends in sludge and air temperature during the drying cycle. Thermocouple data shows a slow climb in sludge temperatures during the drying cycle, as the sludge dried upward from the bottom. Bottom and middle layer sludge temperatures increased 8.5 and 10.4 °F, respectively, while upper sludge temperature increased only 4.0 °F over the drying cycle. During the drying cycle, the general trend observed was that the inlet temperature decreased as the outlet temperature increased. Visual observation of the sludge after the drying cycle indicated the corners and the bottom sludge cake was drying, while the top portion remained wet. This demonstrates a lack of air flow in the upper sludge layer and, therefore, minimal heat transfer due to poor air movement through the poorly dewatered sludge cake.

As with the OO-ALC test events, the lack of drying between the pre and post sludge samples for the LBNL test event is a result of the high moisture content of the poorly dewatered filter cake released from the IWTP press. The hydrated solids eliminates the porous surface area of the sludge required for adequate ventilation. Sludge drying effectiveness is a function of the rapid heat transfer between the recirculated air flow and solids with increasing surface area. One option for drying hydrated solids is to blend the wet filter cake from the press with previously dried sludge in the hopper to improve air movement.

2. Potential for Cross-Media Pollution

a. **Results for OO-ALC.** Sludge samples from the OO-ALC JWI sludge dryer were collected and analyzed to determine the VOC concentrations in the solids. Analysis of the sludge samples provided the background information required to assess the potential for cross-media contamination in the air and water waste streams from the dryers. Toluene and 1,2,4-Trimethylbenzene were detected in the sludge, condensate, and air samples collected from the dryer unit. Table 19 presents the VOC concentrations in the sludge for the two test events.

TABLE 19. VOLATILE ORGANIC COMPOUNDS IN SLUDGE, OO-ALC SLUDGE DRYER TEST.

Compound	Run #1 (9-16-97) ppb		Run #2 (9-17-97) ppb	
	Pre	Post	Pre ^a	Post
p-Isopropyltoluene	3,500	2,900	3,750	4,100
Toluene	31,000	20,000	13,750	18,000
1,2,4-Trimethylbenzene	3,700	2,400	3,400	3,900
1,3,5-Trimethylbenzene	2,600	2,000	2,300	3,000
Xylenes	1,000	ND ^b	800	ND

^a Duplicate samples were collected prior to the start of Run 2. Results are an average of both samples collected.

^b ND = Not detected.

The results of Run #1 show a reduction in the concentration of VOCs in the sludge, as expected, as the sludge is dried. Run #2, however, shows an increase in the concentration of the VOCs detected. These increases are believed to be a result of the difficulty in collecting representative sludge samples. The Run #2 post-drying sample may have consisted of a greater percentage of the wet sludge from the top-middle portion of the cart.

The condensate from the OO-ALC sludge dryer was also analyzed for VOC content. The majority of the VOCs analyzed in the condensate samples were reported as non-detected. The detected compounds were at levels slightly above the minimum detection limits (MDLs). Toluene was reported in four of the five samples collected. Table 20 presents the VOC concentrations for the condensate from the OO-ALC sludge dryer tests.

TABLE 20. VOLATILE ORGANIC COMPOUNDS IN CONDENSATE, OO-ALC SLUDGE DRYER TEST.

Compound	Run #1 (9-16-98) ppbv			Run #2 (9-17-98) ppbv		
	Start	Middle	End	Start ^a	Middle	End
Hexachlorobutadiene	NA ^b	2.5	ND ^c	ND	ND	ND
p-Isopropyltoluene	NA	ND	ND	ND	ND	2.6
Naphthalene	NA	ND	ND	ND	ND	6.4
Toluene	NA	13	ND	7.1	9.0	6.4
1,2,4-Trimethylbenzene	NA	ND	ND	ND	ND	3.5

^a Duplicate sample collected at start of Run 2. Results are an average of both samples collected.

^b NA = Not analyzed. Sample container broke in shipment to laboratory.

^c ND = Not detected.

The flowrate exiting the system from gaps between the sludge dryer and the cart was determined using a hot wire anemometer. Test personnel detected small leaks at the inlet of the cart where the dryer loop enters the bottom of the cart. Leaks were detected and measured at 40 to 100 fpm on both tests. The leaks escaped through small gaps, approximately 1/16 to 1/8 inch wide. The gaps are a result of wear on the foam seal between the cart and the inlet connection from the dryer. Overall, the leaks measured from the dryers were minimal and could be prevented with routine maintenance.

Several VOCs were detected in the dryer loop and near the dryer at concentrations just above detection limits. Toluene was detected at a concentration of 500 ppbv, still well below the OSHA permissible exposure limit of 100 ppmv. The background sample was collected to assess the VOC concentration levels in Building 577 at OO-ALC. Test personnel noted background odors on the site visit and during testing. VOC concentrations detected in the background sample are believed to come from sources other than the dryers. The filter press and several holding tanks are also located in Building 577 next to the dryers. Table 21 shows the VOC concentrations in the recirculating air of the OO-ALC sludge dryer for the two test events.

**TABLE 21. VOLATILE ORGANIC COMPOUNDS IN DRYER AIR, OO-ALC
SLUDGE DRYER TEST.**

Compound	Inlet #1 9-16-97 (ppbv)	Outlet #1 9-16-97 (ppbv)	Near Dryer ^a 9-16-97 (ppbv)	Background 9-16-97 (ppbv)	Inlet #2 9-17-97 (ppbv)	Outlet #2 9-17-97 (ppbv)
Methylene Chloride	6.0	5.8	5.1	5.2	60	64
1,1,1-Trichloroethane	14	15	2.4	ND ^b	10	12
Toluene	510	500	77	16	360	400
m,p-Xylene	15	15	4.3	3.1	17	17
o-Xylene	6.1	6.3	1.7	1.2	6.3	7.2
1,3,5-Trimethylbenzene	19	18	3.0	ND	23	28
1,2,4-Trimethylbenzene	33	33	5.3	1.5	42	46
1,4-Dichlorobenzene	4.4	4.3	ND	ND	4.8	4.8
1,2-Dichlorobenzene	5.5	5.2	ND	ND	5.6	5.9
Acetone	66	78	11	8.6	60	72
2-Butanone (MEK)	73	75	16	6.2	21	22
4-Ethyltoluene	26	26	ND	ND	34	36

^a This sample was collected near small leaks detected in the dryer loop.

^b ND = Not detected.

b. Results for LBNL. There were no volatile organics detected in the LBNL JWJ dryer condensate or sludge. However, the detection limit of the first condensate sample was 20 times higher than normal due to interference from a high non-target compound (tentatively identified as tetrahydrofuran at 15-20 ppm). The higher detection limit would mask low level detections of other compounds, if present. Table 22 presents the VOC concentrations in the condensate and sludge during the LBNL JWJ sludge dryer test event.

Five volatile organic compounds were detected in the LBNL sludge dryer air at levels slightly above detection limit. Table 23 shows the VOC concentration in the recirculating air for the LBNL sludge dryer test.

The JWJ sludge dryer at LBNL is located outside, in a covered cage pad area. Since any leakage of air exiting the system from gaps between the sludge dryer and the cart was to the outside atmosphere, the flowrate of leakage from the dryer was not measured. No leak or background air samples were collected for VOC analyses. Observations during the pre-test site visit and testing indicate that no background odor was evident.

TABLE 22. VOLATILE ORGANIC COMPOUNDS IN CONDENSATE AND SLUDGE, LBNL JWI SLUDGE DRYER TEST.

Compound	Start Cycle	Mid-Cycle	End Cycle
Condensate (µg/L)			NS ^a
Benzene			
Toluene	ND ^b (< 40)	ND(< 2)	
Xylene	ND(< 40)	ND(< 2)	
Total VOC as 8260 Analytes	ND(< 40)	ND(< 2)	
	ND	ND	
Sludge (µg/kg)		NS	
Benzene			
Toluene	ND(< 100)		ND(< 100)
Xylene	ND(< 100)		ND(< 100)
Total VOCs as 8260 Analytes	ND(< 100)		ND(< 100)
	ND		ND

^aNS= Not sampled.

^bND = Not detected.

TABLE 23. VOLATILE ORGANIC COMPOUNDS IN AIR, LBNL SLUDGE DRYER TEST.

Compound	Inlet Conc. (ppbv)	Outlet Conc. (ppbv)	Blank Conc. (ppbv)
Acetone	< 5.3	6.7	ND ^a
Benzene	< 1.1	1.1	ND
Toluene	1.2	1.2	ND
m,p-Xylene	1.5	1.7	ND
Methylene chloride	1.2	1.5	0.18

^a ND = Not detected.

Methylene chloride was detected in both inlet and outlet TO-14 air samples, but is not considered present as a sample contaminant. Methylene chloride was also found in the background blank analyses, and is considered a common laboratory contaminant.

3. Economic Analysis

Table 24 presents the dryer electricity usage for the two dryers at OO-ALC and LBNL. The estimated average operating cost per drying cycle for the OO-ALC system was \$70. The estimated average operating cost for the LBNL system was \$53 per drying cycle. This is

based on an estimated local utility energy cost of \$0.116/KWH, average amperage, and assumes a drying cycle of 12 hours. One man-hour for system operation per batch was assumed. A loaded hourly labor rate of \$52.00 was used to determine system labor costs. This figure was based on an average wage of \$16.49 per hour for a military or civilian system operator, multiplied by overhead costs.

TABLE 24. ELECTRICITY USAGE, LOW TEMPERATURE SLUDGE DRYING TESTS.

Amperage	OO-ALC Test #1 (amps, 3 lines)	OO-ALC Test #2 (amps, 3 lines)	LBNL (amps, 2 lines)
Minimum	96.0	99.2	2.7
Maximum	110.3	180.0	16.6
Average	104.5	117.1	4.5

As part of the economic analysis performed on the dryer units, the maintenance requirements of the units were also evaluated. The following maintenance schedule is recommended by the manufacturer:

- Inspect air intake filter weekly, clean or replace as needed.
- Inspect evaporator coil weekly and clean any accumulated sludge particles from tubes.
- Inspect air hoses and gaskets monthly for holes or tears.
- Grease hopper casters monthly.
- Check refrigerant system, charge on an annual basis with R-22 freon.

In general, the labor and maintenance requirements to operate these units are very minimal.

E. CONCLUSIONS

The sludge drying effectiveness of the JWI J-Mate dryers is dependent on the initial moisture content of the sludge filter cake released from the IWTP filter press. None of the three sludge dryer test events met the target disposal moisture content of 70 percent solids. However, the sludge tested in the JWI dryers had a pre-test dry solids content of 13-20 percent (after discharge from the IWTP filter press). Typically sludge moisture content of the filter cake received from the filter press is approximately 30-40 percent solids. The JWI dryers should

typically dry a filter cake of 30 percent solids to 80 percent solids. This study tested a worse-case scenario, and did not adequately reflect the effectiveness of the dryers under normal operating conditions. It was determined that the JWI dryer requires the sludge in cake form from the filter press for efficient draining and even drying.

The JWI dryer potential for cross-media pollution is minimal. There were no significant leaks detected in the air flow system. VOC concentrations in the exhaust air and the condensate were negligible at slightly above detectable limits.

The JWI J-Mate dryers are potentially economical, using the low-cost electric heat source. However, insufficient data were collected in this study to allow drawing firm conclusions. The simple unit working parts and control system allows for effortless operation and low maintenance. A disadvantage to the JWI sludge dryer system is a cycle drying time at 12 hours minimum. However, limited operator labor is needed during that drying time. The low energy usage of the JWI dryer system and minimal operator attention during the drying cycle accounts for its cost effectiveness.

F. RECOMMENDATIONS

Since sludge drying effectiveness by low temperature sludge dryers varies with the moisture of the material, additional field tests drying sludge cakes with the accepted 30-40 percent solids content is recommended for proper evaluation.

The JWI J-Mate sludge dryers may be an economical method of dewatering the IWTP sludge cake, and thus reducing the volume and cost of hazardous waste disposal.

The JWI J-Mate sludge dryers were also effective at eliminating pollutant emissions to the atmosphere during the drying cycle. The closed loop system eliminates air emissions, while the low temperature drying cycle results in energy savings.